

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|--|----|--|
| (51) International Patent Classification ⁶ : C11D 3/50, 3/37 | A1 | (11) International Publication Number: WO 99/21954 (43) International Publication Date: 6 May 1999 (06.05.99) |
| (21) International Application Number: PCT/IB98/01632 (22) International Filing Date: 19 October 1998 (19.10.98) (30) Priority Data: 60/063,709 29 October 1997 (29.10.97) US | | (81) Designated States: BR, CA, CN, JP, MX, NO, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> |
| (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). | | |
| (72) Inventor; and (75) Inventor/Applicant (for US only): SAWICKI, Edward, Mack [US/US]; 7675 Indian Pond Court, Cincinnati, OH 45241 (US). | | |
| (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). | | |
| (54) Title: LAUNDRY COMPOSITIONS HAVING REDUCED MALODOR AND METHODS FOR PROVIDING THE SAME | | |
| (57) Abstract | | |
| <p>The present invention relates to methods for obtaining laundry detergent and fabric softening compositions which have reduced malodor. The present invention comprises the step of combining a laundry detergent or fabric softener composition with a fragrance pro-accord capable of releasing one or more fragrance raw materials on a delayed basis which serve to mask malodors which may develop.</p> | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|---------------------------------------|----|---|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakhstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

LAUNDRY COMPOSITIONS HAVING
REDUCED MALODOR AND
METHODS FOR PROVIDING THE SAME

FIELD OF THE INVENTION

The present invention relates to laundry detergent, fabric softener and fabric appearance compositions having reduced malodor and to methods for providing said compositions. The reduced malodor compositions of the present invention comprise an effective amount of a pro-accord material which effectively masks the degradation products typical of fabric softener actives.

BACKGROUND OF THE INVENTION

Laundry detergent and fabric softener compositions comprise active ingredients *inter alia* surfactants, diester and diamide quaternary ammonium compounds all of which are derived from fatty acids. Fatty acids and materials made from fatty acid sources, especially those having one or more sites of unsaturation, degrade over time due to the effects of oxygen as well as other factors. In fact, the breakdown of fatty acids is attributed to the "spoiled" or "rancid" odor associated with lard, vegetable oils, etc. no longer deemed fit for human consumption.

Laundry detergent and fabric softener compositions, whether liquid rinse-added or substrate-added (i.e. dryer sheets), also develop malodors due to the breakdown of materials which are comprised of fatty acid moieties. One proposed remedy has been the inclusion of perfumes and other fragrance raw materials into the compositions to mask the objectionable odor. In order for a material to be effective as a perfume or fragrance it must be volatile enough to be "smelled". However, it is because of the high volatility of perfume ingredients that laundry detergent compositions and fabric softener compositions become depleted of masking scents long before the formation of malodors occurs later in the shelf life of the product.

In addition, fabric softener compositions are typically acidic (pH from 2.5 to 5.5) while laundry detergent compositions are alkaline (pH from 8 to about 11). Therefore, a perfume ingredient or masking agent which is effective in one pH range may be ineffectual in another. In addition, the formulator must consider the synergy that perfume raw materials and masking agents might have with other adjunct ingredients which make up the laundry or fabric conditioning compositions. Therefore, the fact that a material may serve as effective malodor control masking agent in a fabric softener composition does not mean the same material will be effective in a laundry detergent composition.

Accordingly, there remains a need in the art for compounds which mask malodors and methods for masking these malodors with form in all types of laundry detergent and fabric softener compositions. Indeed, there is a long felt need to have a method for controllably releasing a fragrance raw material or odor masking agent which provides the consumer with confidence that a laundry detergent or fabric softening composition is still effective.

BACKGROUND ART

The following relate to the subject matter of fragrance ingredients. U.S. 5,626,852 Suffis *et al.*, issued May 6, 1997; U.S. 5,232,612 Trinh *et al.*, issued August 3, 1996; U.S. 5,506,201 McDermott *et al.*, issued April 9, 1996; U.S. 5,378,468 Suffis *et al.*, issued January 3, 1995; U.S. 5,266,592 Grub *et al.*, issued November 30, 1993; U.S. 5,081,111 Akimoto *et al.*, issued January 14, 1992; U.S. 4,994,266 Wells, issued February 19, 1991; U.S. 4,524,018 Yemoto *et al.*, issued June 18, 1985; U.S. 3,849,326 Jaggers *et al.*, issued November 19, 1974; U.S. 3,779,932 Jaggers *et al.*, issued December 18, 1973; JP 07-179,328 published July 18, 1995; JP 05-230496 published September 7, 1993; WO 96/14827 published May 23, 1996; WO 95/04,809 published February 16, 1995; and WO 95/16660 published June 22, 1995. In addition, P.M. Muller, D. Lamparsky Perfumes Art, Science, & Technology Blackie Academic & Professional, (New York, 1994) is included herein by reference.

SUMMARY OF THE INVENTION

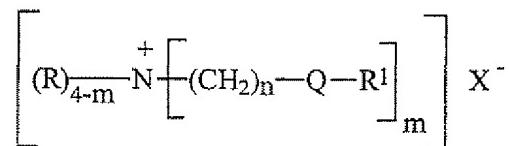
The present invention meets the aforementioned needs in that it has been surprisingly discovered that fragrance raw materials can serve to mask the formation of malodors in laundry detergent compositions, fabric softener compositions, and the like and that these materials are deliverable in a releasable and sustainable manner by the inclusion of certain pro-accords into the laundry formulation. The pro-accords act to slowly release fragrance raw materials which are volatile enough to be aesthetically appreciated while being strong enough to mask the malodors which can form during certain storage and usage conditions. However, because there is a continuous release of fragrance raw materials over time by the pro-accords, the pleasurable scent does not dissipate or evaporate in a manner similar to free perfumes and fragrance materials. In fact, the formulator by applying the conditions set forth in the present specification can design pro-accord molecules which will continue to release fragrance raw materials for varying lengths of time. Also, the fragrance raw materials releasable by the pro-accords of the present invention, may be any fragrance raw material convertible to a releasable pro-accord *inter alia* aldehydes, ketones, alcohols, terpenes, and esters.

A first aspect of the present invention relates to a method for providing a laundry detergent compositions having reduced development of malodor, comprising the step of adding an effective amount of a pro-accord to a laundry detergent composition comprising:

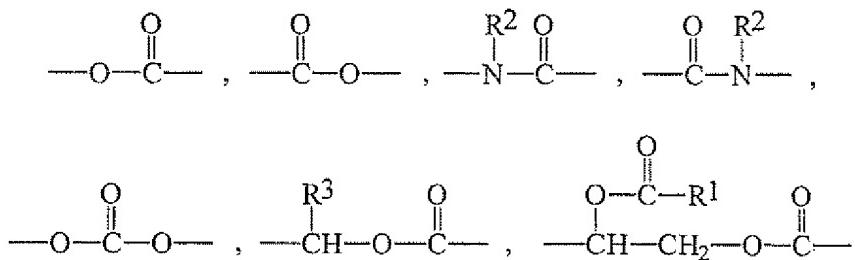
- a) at least about 0.01% by weight, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a detergents surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant;
- b) the balance carriers and adjunct ingredients, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

A further aspect of the present invention relates to a method for providing a fabric softener compositions having reduced development of malodor, comprising the step of adding an effective amount of a pro-accord to a fabric softener composition comprising:

- a) at least about 2%, preferably from about 2%, more preferably from about 3% to about 60%, more preferably to about 40% by weight, of a fabric softening active having the formula:



wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:



wherein R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; R³ is hydrogen, C₁-C₄ alkyl, and mixtures thereof; X is a softener compatible anion; m is from 1 to 3; n is from 1 to 4; and

- b) the balance carriers and adjunct ingredients, said adjunct ingredients selected from the group consisting of nonionic fabric softening agents, concentration aid, soil release agent, perfume, preservatives, stabilizers, colorants, optical brighteners, opacifiers, fabric conditioning agents, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, cationic charge boosters, and mixtures thereof.

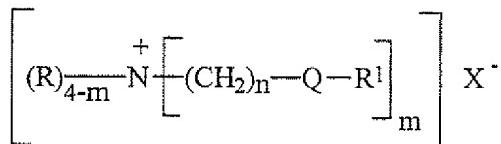
The present invention yet further relates to laundry detergent compositions comprising:

- a) an effective amount of a pro-accord;
- b) at least about 0.01% by weight, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a detergents surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant;
- c) the balance carriers and adjunct ingredients, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

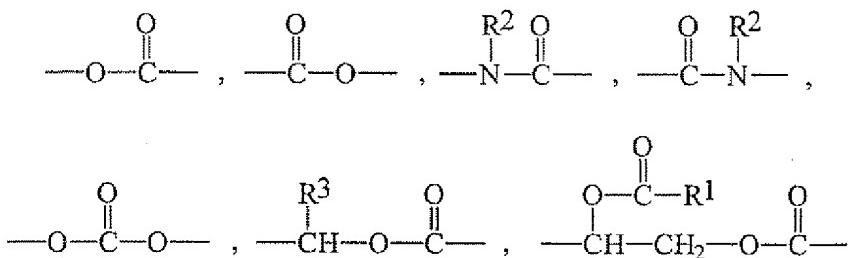
The present invention also further relates to fabric softener compositions having reduced development of product malodor, comprising:

- a) an effective amount of a pro-accord;

- b) at least about 2%, preferably from about 2%, more preferably from about 3% to about 60%, more preferably to about 40% by weight, of a fabric softening active having the formula:



wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:



wherein R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; R³ is hydrogen, C₁-C₄ alkyl, and mixtures thereof; X is a softener compatible anion; m is from 1 to 3; n is from 1 to 4; and

- c) the balance carriers and adjunct ingredients, said adjunct ingredients selected from the group consisting of nonionic fabric softening agents, concentration aid, soil release agent, perfume, preservatives, stabilizers, colorants, optical brighteners, opacifiers, fabric conditioning agents, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, cationic charge boosters, and mixtures thereof.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for providing low or nil malodor laundry detergent and fabric softener compositions, said method comprising the step of adding to a laundry detergent or fabric softener composition one or more pro-fragrances or pro-accords which are capable of releasing one or more fragrance raw materials during the course of the laundry detergent or fabric softener composition shelf life. It is not uncommon that after formulation laundry detergent and fabric softener compositions slowly begin forming malodors. While not wishing to be limited by theory, in many cases, especially under the circumstances where fatty acids have been used as starting materials to prepare deterotive surfactants, Diester Quaternary Ammonium compounds (DEQA's), and other triglyceride-based compounds, these fatty acyl unit containing molecules can begin to oxidize and/or hydrolyze under certain storage and usage conditions, especially under the liquid alkaline conditions of certain laundry detergent compositions and the acidic conditions typical of fabric softener formulations. This is especially true when the fatty acyl units contain sites of unsaturation. The fatty acids which are released by this degradation process may ultimately include fatty acids which have a low odor threshold as well as a foul scent.

This problem is overcome by admixing, in addition to any other desired perfume or fragrance raw materials, one or more pro-fragrances or pro-accords according to the present invention. Each pro-accord, depending upon which fragrance raw materials comprise the pro-accord and upon the pro-accord structure, will have a separate differential release rate and aroma or smell. The formulator, by judicious assembly of the pro-accord molecule itself, can provide a sustained release of fragrance to a laundry detergent or fabric softener composition for up to several months past the normal product turnover time and thus prolong the storage life time of the product composition. In addition, formulation of quicker releasing pro-accords with pro-accords having a delayed or more sustained release can provide a product having a mixture of different scents as well as providing variable levels of released fragrance. For example, a product may be formulated to degrade such that initially low levels of fragrance raw materials are present, but at a time when the degradation of fatty acyl groups are more likely to form malodors, higher levels of fragrances are released. For some formulations, a specific delayed release of a particular fragrance raw material may be used to signal the end of suitable shelf life or other product variables.

Some pro-fragrances have been formulated for delivery of their fragrance raw materials after the pro-fragrance or pro-accord has been effectively delivered to a fabric surface or, in some cases, to human skin or hair. However, the pro-accords of the present invention slowly release their perfume raw materials as the product is stored in the

original container in essentially the original compositional form. This slow release extends the usable shelf life of laundry and fabric softening compositions. Typically these products are stable over an extended period of time, in fact, far beyond the time in which the first malodorous materials are formed.

The malodorous compounds have a very low odor threshold, therefore, only a very small amount of material need degrade into a malodorous material in order for the unpleasant smell to be perceptible to the consumer. Many consumers incorrectly associate a malodorous smell as a signal that a material is now no longer "effective". The ability to misconstrue that a laundry or fabric softening composition is "beyond shelf life" due to malodorous materials is therefore overcome by the present invention.

The pro-fragrances and pro-accords of the present invention begin delivering the fragrance raw materials in a slow and controlled manner once admixed within the final formulation, or upon activation, for example, placed in to a warehouse having a temperature above a critical temperature limit which facilitates degradation of the ingredients which lead to malodor formation.

For the purposes of the present invention the term "pro-fragrance" is defined as "pro-accord which is designed to release a single fragrance raw material" whereas a "pro-accord" is defined as "material which releases two or more fragrance raw materials". However, for the purposes of the present invention, because some fragrance releasing materials serving as a "pro-fragrance" in one embodiment can equally serve as a "pro-accord" in a different embodiment, the term "pro-fragrance" is used interchangeably with the term "pro-accord" and either term may be used to stand equally well for any fragrance releasing compound described herein singly or collectively.

For the purposes of the present invention "fragrance raw materials" are herein defined as compounds imparting an odor, fragrance, essence, or scent either alone or in combination with other "fragrance raw materials" which is considered aesthetically pleasing, preferably said compounds have a molecular weight of at least 100 g/mol.

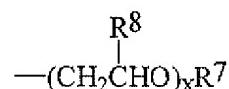
The pro-accord containing compositions of the present invention can comprise any number of pro-accords which when taken together are capable of releasing complex perfume fragrances. However, in some instances the fragrance releasing pro-accords of the present invention are capable of undergoing chemical transformation and thereby releasing one or more fragrance raw materials in addition to the fragrance raw materials used to prepare the original parent pro-accord. In addition, the pro-fragrances and pro-accords of the present invention are suitable for delivery of any type of fragrance "characteristic" desired by the formulator.

The following describe the fragrance releasing pro-accords and pro-fragrances of the present invention.

Pro-Accords and Pro-Fragrances

For the purposes of the present invention the term "substituted" as it applies to linear alkyl, branched alkyl, cyclic alkyl, linear alkenyl, branched alkenyl, cyclic alkenyl, branched alkoxy, cyclic alkoxy, alkynyl, and branched alkynyl units are defined as "carbon chains which comprise substituents other than branching of the carbon atom chain", for example, other than the branching of alkyl units (e.g. isopropyl, isobutyl). Non-limiting examples of "substituents" include hydroxy, C₁-C₁₂ alkoxy, preferably methoxy; C₃-C₁₂ branched alkoxy, preferably isopropoxy; C₃-C₁₂ cyclic alkoxy; nitrilo; halogen, preferably chloro and bromo, more preferably chloro; nitro; morpholino; cyano; carboxyl, non-limiting examples of which are -CHO; -CO₂M⁺, -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl); -SO₃⁻M⁺; -OSO₃⁻M⁺; -N(R¹⁰)₂; and -N^{+(R¹⁰)₃X⁻ wherein each R¹⁰ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; wherein M is hydrogen or a water soluble cation; and X is chlorine, bromine, iodine, or other water soluble anion.}

For the purposes of the present invention substituted or unsubstituted alkyleneoxy units are defined as moieties having the formula:



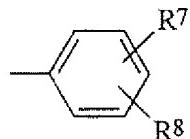
wherein R⁷ is hydrogen; R⁸ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 10.

For the purposes of the present invention substituted or unsubstituted alkyleneoxyalkyl are defined as moieties having the formula:

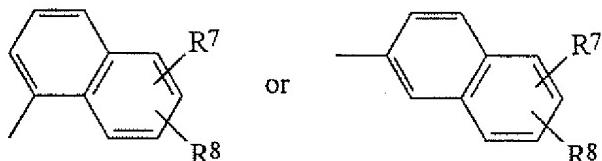


wherein R⁷ is hydrogen, C₁-C₁₈ alkyl, C₁-C₄ alkoxy, and mixtures thereof; R⁸ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 10 and the index y is from 2 to about 18.

For the purposes of the present invention substituted or unsubstituted aryl units are defined as phenyl moieties having the formula:

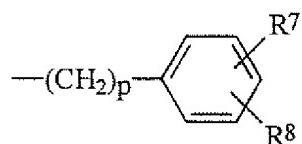


or α and β -naphthyl moieties having the formula:



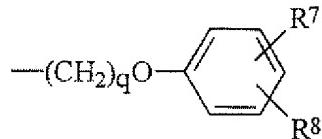
wherein R⁷ and R⁸ can be substituted on either ring, alone or in combination, and R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₄ alkoxy, C₃-C₆ branched alkoxy, nitrilo, halogen, nitro, morpholino, cyano, carboxyl (-CHO; -CO₂⁻M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), -SO₃⁻M⁺, -OSO₃⁻M⁺, -N(R¹⁰)₂, and -N⁺(R¹⁰)₃X⁻ wherein each R¹⁰ is independently hydrogen, C₁-C₄ alkyl, or mixtures thereof; and mixtures thereof, R⁷ and R⁸ are preferably hydrogen, C₁-C₆ alkyl, -CO₂⁻M⁺, -SO₃⁻M⁺, -OSO₃⁻M⁺, and mixtures thereof; more preferably R⁷ or R⁸ is hydrogen and the other moiety is C₁-C₆; wherein M is hydrogen or a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion. Examples of other water soluble anions include organic species such as fumarate, succinate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like.

For the purposes of the present invention substituted or unsubstituted alkylenearyl units are defined as moieties having the formula:



wherein R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂⁻M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof, p is from 1 to about 14; M is hydrogen or a water soluble cation.

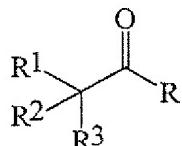
For the purposes of the present invention substituted or unsubstituted alkyleneoxyaryl units are defined as moieties having the formula:



wherein R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂⁻M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof, q is from 1 to about 14; M is hydrogen or a water soluble cation.

β-Ketoesters

The compositions according to the present invention may comprise one or more β-ketoesters having the formula:



wherein R is alkoxy derived from a fragrance raw material alcohol. Non-limiting examples of preferred fragrance raw material alcohols include 2,4-dimethyl-3-cyclohexene-1-methanol (Floralol), 2,4-dimethyl cyclohexane methanol (Dihydro floralol), 5,6-dimethyl-1-methylethenylbicyclo[2.2.1]hept-5-ene-2-methanol (Arbozol), α,α,-4-trimethyl-3-cyclohexen-1-methanol (α-terpineol), 2,4,6-trimethyl-3-cyclohexene-1-methanol (Isocyclo geraniol), 4-(1-methylethyl)cyclohexane methanol (Mayol), α-3,3-trimethyl-2-norborane methanol, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methanol, 2-phenylethanol, 2-cyclohexyl ethanol, 2-(o-methylphenyl)-ethanol, 2-(m-methylphenyl)ethanol, 2-(p-methylphenyl)ethanol, 6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-ethanol (nopol), 2-(4-methylphenoxy)-ethanol, 3,3-dimethyl-Δ²-β-norbornane ethanol (patchomint), 2-methyl-2-cyclohexylethanol, 1-(4-isopropylcyclohexyl)-ethanol, 1-phenylethanol, 1,1-dimethyl-2-phenylethanol, 1,1-dimethyl-2-(4-methylphenyl)ethanol, 1-phenylpropanol, 3-phenylpropanol, 2-phenylpropanol (Hydrotropic Alcohol), 2-(cyclododecyl)propan-1-ol (Hydroxy-ambran), 2,2-dimethyl-3-(3-methylphenyl)-propan-1-ol (Majantol), 2-methyl-3-phenylpropanol, 3-phenyl-2-propen-1-ol (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-ol (methylcinnamyl alcohol), α-n-pentyl-3-phenyl-2-propen-1-ol (α-amyl-cinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propanol, 3-(4-methylcyclohex-3-ene)butanol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butanol, 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-2-buten-1-ol, 3-methyl-2-buten-1-ol (prenol), 2-methyl-4-(2,2,3-

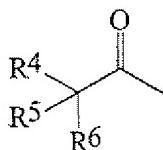
trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, ethyl 3-hydroxybutyrate, 4-phenyl-3-butene-2-ol, 2-methyl-4-phenylbutan-2-ol, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)-butan-2-one, 3-methyl-pentanol, 3-methyl-3-penten-1-ol, 1-(2-propenyl)cyclopentan-1-ol (plinol), 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol (Phenoxyanol), 2-methyl-5-phenylpentanol, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0^(2,6)]hept-3-yl)-2-penten-1-ol (santalol), 4-methyl-1-phenyl-2-pentanol, 5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol (sandalore), (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-ol, 3-methyl-1-phenylpentan-3-ol, 1,2-dimethyl-3-(1-methylethenyl)cyclopentan-1-ol, 2-isopropyl-5-methyl-2-hexenol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 2-isoproenyl-4-methyl-4-hexen-1-ol (Lavandulol), 2-ethyl-2-prenyl-3-hexenol, 1-hydroxymethyl-4-iso-propenyl-1-cyclohexene (Dihydrocuminal alcohol), 1-methyl-4-isopropenylcyclohex-6-en-2-ol (carvenol), 6-methyl-3-isopropenylcyclohexan-1-ol (dihydrocarveol), 1-methyl-4-iso-propenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclohexanol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol (rootanol), 4-isopropyl-cyclohexanol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isobornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1-methyl-4-isopropylcyclohexan-8-ol (dihydroterpineol), 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol, 2,4-dimethylheptan-1-ol, 6-heptyl-5-hepten-2-ol (isolinalool), 2,4-dimethyl-2,6-heptandienol, 6,6-dimethyl-2-oxymethyl-bicyclo[3.1.1]hept-2-ene (myrtenol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol (dimetol), 2,6,6-trimethylbicyclo[1.3.3]heptan-2-ol, octanol, 2-octenol, 2-methyloctan-2-ol, 2-methyl-6-methylene-7-octen-2-ol (myrcenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-octenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-7-methoxyoctan-2-ol (osyrol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-1-ol (pelargol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol (dihydrolinalool), 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol), 2,6-dimethyl-5,7-octadien-2-ol, 4,7-dimethyl-4-vinyl-6-octen-3-ol, 3-methyloctan-3-ol, 2,6-dimethyloctan-2-ol, 2,6-dimethyloctan-3-ol, 3,6-dimethyloctan-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-3,5-octadien-2-ol (muguol), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonanol, 2,6-nonadien-1-ol, *cis*-6-nonene-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonenone, 2-nonen-1-ol, 2,4-nonadien-

1-ol, 3,7-dimethyl-1,6-nonadien-3-ol, decanol, 9-decenol, 2-benzyl-M-dioxa-5-ol, 2-decen-1-ol, 2,4-decadien-1-ol, 4-methyl-3-decen-5-ol, 3,7,9-trimethyl-1,6-decadien-3-ol (isobutyl linalool), undecanol, 2-undecen-1-ol, 10-undecen-1-ol, 2-dodecen-1-ol, 2,4-dodecadien-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-ol (nerolidol), 3,7,11,15-tetramethylhexadec-2-en-1-ol (phytol), 3,7,11,15-tetramethylhexadec-1-en-3-ol (iso phytol), benzyl alcohol, p-methoxy benzyl alcohol (anisyl alcohol), *para*-cymen-7-ol (cuminalcohol), 4-methyl benzyl alcohol, 3,4-methylenedioxy benzyl alcohol, methyl salicylate, benzyl salicylate, *cis*-3-hexenyl salicylate, n-pentyl salicylate, 2-phenylethyl salicylate, n-hexyl salicylate, 2-methyl-5-isopropylphenol, 4-ethyl-2-methoxyphenol, 4-allyl-2-methoxyphenol (eugenol), 2-methoxy-4-(1-propenyl)phenol (isoeugenol), 4-allyl-2,6-dimethoxy-phenol, 4-tert-butylphenol, 2-ethoxy-4-methylphenol, 2-methyl-4-vinylphenol, 2-isopropyl-5-methylphenol (thymol), pentyl-*ortho*-hydroxy benzoate, ethyl 2-hydroxy-benzoate, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 3-hydroxy-5-methoxy-1-methylbenzene, 2-tert-butyl-4-methyl-1-hydroxybenzene, 1-ethoxy-2-hydroxy-4-propenylbenzene, 4-hydroxytoluene, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthol, 2,5,5-trimethyl-octahydro-2-naphthol, 1,3,3-trimethyl-2-norbornanol (fenchol), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-ol, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-ol, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetra-hydrofuran, β -caryophyllene alcohol, vanillin, ethyl vanillin, and mixtures thereof.

More preferably, the fragrance raw material alcohol is selected from the group consisting of *cis*-3-hexen-1-ol, hawthanol [admixture of 2-(o-methylphenyl)-ethanol, 2-(m-methylphenyl)ethanol, and 2-(p-methylphenyl)ethanol], heptan-1-ol, decan-1-ol, 2,4-dimethyl cyclohexane methanol, 4-methylbutan-1-ol, 2,4,6-trimethyl-3-cyclohexene-1-methanol, 4-(1-methylethyl)cyclohexane methanol, 3-(hydroxy-methyl)-2-nonanone, octan-1-ol, 3-phenylpropanol, Rhodinol 70 [3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octenol admixture], 9-decen-1-ol, α -3,3-trimethyl-2-norborane methanol, 3-cyclohexylpropan-1-ol, 4-methyl-1-phenyl-2-pentanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, phenyl ethyl methanol; propyl benzyl methanol, 1-methyl-4-isopropenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol (menthol), 4-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropylcyclo-hexanol, *trans*-decahydro- β -naphthol, 2-tert-butylcyclohexanol, 3-phenyl-2-propen-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol, 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol (dihydrolinalool), 2,6-dimethyl-7-octen-2-ol

(dihydromyrcenol), 4-methoxybenzyl alcohol, benzyl alcohol, 4-allyl-2-methoxyphenol, 2-methoxy-4-(1-propenyl)phenol, vanillin, and mixtures thereof.

R¹, R², and R³ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted aryl, C₂-C₂₀ substituted or unsubstituted alkyleneoxy, C₃-C₂₀ substituted or unsubstituted alkyleneoxyalkyl, C₇-C₂₀ substituted or unsubstituted alkylenearyl, C₆-C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R¹, R², or R³ is a unit having the formula:



wherein R⁴, R⁵, and R⁶ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₁-C₃₀ substituted or unsubstituted linear alkoxy, C₃-C₃₀ substituted or unsubstituted branched alkoxy, C₃-C₃₀ substituted or unsubstituted cyclic alkoxy, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkylenearyl, C₆-C₃₀ substituted or unsubstituted aryl; or R⁴, R⁵, and R⁶ can be taken together to form C₆-C₃₀ substituted or unsubstituted aryl; and mixtures thereof.

In one preferred embodiment of β-ketoesters at least two R², or R³ units are hydrogen and R⁴, R⁵, and R⁶ units are each hydrogen. In another preferred embodiment two R⁴, R⁵, and R⁶ units are hydrogen and the remaining unit is C₁-C₂₀ substituted or unsubstituted linear alkyl, C₃-C₂₀ substituted or unsubstituted branched alkyl, C₃-C₂₀ substituted or unsubstituted cyclic alkyl; more preferably hexyl, heptyl, octyl, nonanyl, ω-hexenyl, ω-heptenyl, ω-octenyl, ω-nonenyl, and mixtures thereof. Also preferably R⁴, R⁵, and R⁶ are taken together to form a C₆-C₃₀ substituted or unsubstituted aryl unit, preferably substituted or unsubstituted phenyl and naphthyl. Also preferred embodiments include providing R² and R³ moieties which provide

increased fabric substantivity or which facilitate the rate at which fragrance raw materials are released.

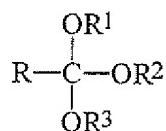
Non-limiting examples of ketones which are releasable by the β -ketoester pro-accords of the present invention are α -damascone, β -damascone, δ -damascone, β -damascenone, muscone, 3,3-dimethylbutanone, methyl phenyl ketone (acetophenone), 4-phenylbutan-2-one (benzyl acetone), 2-acetyl-3,3-dimethyl norbornane (camek dh), 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H) indanone (cashmeran), 4-(1,3)-benzodioxol-5-yl 3-buten-2-one (cassione), 4-(3,4-methylenedioxyphenyl)-2-butanone (dulcanyl), 3-octanone, 6-acetyl-1,2,3,4-tetrahydronaphthalene ketone (florantone t), ethyl-2-n-hexyl acetoacetate (gelsone), 2,6-dimethylundeca-2,6-dien-10-one, 6,10-dimethyl-5,9-undecadien-2-one, 3,3-dimethylcyclohexyl methyl ketone (herbac), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β -ionone), 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α -ionone), 3-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (δ -methyl ionone), 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one (γ -methyl ionone), 3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (irisantheme), 4-(2,3,5-trimethyl-4-cyclohexen-1-yl)-3-buten-2-one (iritone), 4-methyl-(2,5,6,6-tetramethyl-2-cyclohexen-1-yl)-3-buten-2-one (α -ionone), 1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-acetonaphthone (iso cyclomone e), 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene (Iso E Super®), acetyl diisoamylene (Koavone®), methyl amyl ketone, 2-acetonaphthone cedr-8-enyl methyl ketone (methyl cedrylone), 2,3,6-trimethyl-cyclohexen-4-yl-1-methyl ketone (methyl cyclo citrone), hexahydroacetophenone (methyl cyclohexyl ketone), 6-methyl-3,5-heptadien-2-one, 6-methyl-5-hepten-2-one, 2-octanone, 3-(hydroxymethyl)-2-nonanone, 4-acetyl-1,1-dimethyl-6-tert-butyl indane (musk indanone), 2,6-dinitro-3,5-dimethyl-4-acetyl-tert-butyl benzene (musk ketone), 1-para-menthen-6-yl propanone (nerone), para-methoxy acetophenone (acetanisole), 6-acetyl-1,1,2,3,3,5-hexamethyl indan (Phantolid®), 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin (Tonalid®, Musk Plus®), 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane (Traseolide 70®), methyl-2,6,10-trimethyl-2,5,9-cyclododecatriene-1-yl ketone (Trimofix O®), methyl cedrylone (Vertofix Coeur®), 4-(4-hydroxy-3-methoxyphenyl)-2-butanone, *cis*-jasmine, dihydrojasmine, α -ionone, β -ionone, dihydro- β -ionone, 4-(4-hydroxyphenyl)butan-2-one, *l*-carvone, 5-cyclohexadecen-1-one, decatone, 2-[2-(4-methyl-3-cyclohexenyl-1-yl)propyl]cyclopentan-2-one, 2-sec-butylcyclohexanone, allyl ionone, α -acetone, geranyl acetone, 1-(2-methyl-5-isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisoamylene, methyl cyclocitron, 4-*t*-pentyl cyclohexanone, p-*t*-butylcyclohexanone, o-*t*-

butylcyclohexanone, menthone, methyl-7,3-dihydro-2H-1,5-benzodioxepine-3-one, fenchone, methyl hydroxynaphthyl ketone, and mixtures thereof.

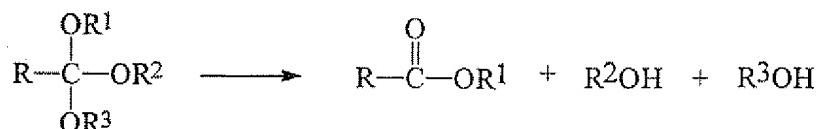
Examples of preferred pro-fragrances which comprise the fragrance delivery systems of the present invention include 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(4-nitrophenyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(β -naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(4-methoxyphenyl)-3-oxo-propionate, (α,α -4-trimethyl-3-cyclohexenyl)methyl 3-(β -naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(α -naphthyl)-3-oxo-propionate, *cis* 3-hexen-1-yl 3-(β -naphthyl)-3-oxo-propionate, 9-decen-1-yl 3-(β -naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate, 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, 2,6-dimethyl-7-octen-2-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2,2-dimethylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-2,6-octadienyl 3-(β -naphthyl)-3-oxo-propionate, 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate, and mixtures thereof.

Orthoesters

Another class of compounds useful as pro-accords according to the present invention are orthoesters having the formula:



wherein typically hydrolysis of the orthoester releases fragrance raw material components according to the following scheme:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, preferably the moieties which substitute the aryl units are alkyl moieties, and mixtures thereof, preferably R is hydrogen, methyl, ethyl, and phenyl. R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear,

branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof.

Orthoester Releasable Components: Hydrolysis of the orthoesters of the present invention have two types of releasable components, namely alcohols and esters. Hydrolysis of an orthoester will yield two equivalents of releasable alcohol, preferably a primary or secondary alcohol and one equivalent of releasable ester. The released ester, when taken together with the released alcohol, forms a binary fragrance accord. For example tri-geranyl orthoformate releases the binary accord geraniol/geranyl formate.

Preferred esters which are releasable components of the orthoesters of the present invention included but are not limited to geranyl formate, citronellyl formate, phenylethyl formate, phenoxyethyl formate, *trans*-2-hexenyl formate, *cis*-3-hexenyl formate, *cis*-6-nonenyl formate, 9-decenyl formate, 3,5,5-trimethylhexyl formate, 3-methyl-5-phenylpentanyl formate, 6-methylheptan-2-yl formate, 4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl formate, 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl formate, 4-isopropylcyclohexyleth-2-yl formate, 6,8-dimethylnonan-2-yl formate, decahydro-β-naphthyl formate, 4-isopropylcyclohexylmethyl formate, linalyl formate, lavandulyl formate, citronellyl formate, α-terpinyl formate, nopyl formate, isobornyl formate, bornyl formate, isobornyl formate, guaiyl formate, 2-*tert*-butylcyclohexyl formate, 4-*tert*-butylcyclohexyl formate, decahydro-β-naphthyl formate, menthyl formate, p-menthanyl formate, neryl formate, cinnamyl formate, ethyl acetate, butyl acetate, isoamyl acetate, hexyl acetate, 3,5,5-trimethylhexyl acetate, geranyl acetate, citronellyl acetate, phenylethyl acetate, phenoxyethyl acetate, *trans*-2-hexenyl acetate, *cis*-3-hexenyl acetate, *cis*-6-nonenyl acetate, 9-decenyl acetate, 3-methyl-5-phenylpentanyl acetate, 6-methyl-heptan-2-yl acetate, 4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl acetate, 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl acetate, decahydro-β-naphthyl acetate, menthyl acetate, benzyl acetate, 4-isopropylcyclohexyleth-2-yl acetate, 6,8-dimethylnonan-2-yl acetate, 1-phenylethyl acetate, 4-isopropylcyclohexylmethyl acetate, linalyl acetate, lavandulyl acetate, citronellyl acetate, α-terpinyl acetate, nopyl acetate, isobornyl acetate, bornyl acetate, isobornyl acetate, guaiyl acetate, 2-*tert*-butylcyclohexyl acetate, 4-*tert*-butylcyclohexyl acetate, decahydro-β-naphthyl acetate, menthyl acetate, p-menthanyl acetate, neryl acetate, cinnamyl acetate, ethyl propionate, ethyl butyrate, butyl butyrate, isoamyl

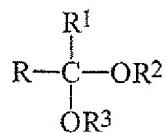
butyrate, hexyl butyrate, *cis*-3-hexenyl butyrate, *cis*-3-hexenyl isobutyrate, ethyl isovalerate, 2-methylbutyrate, ethyl hexanoate, 2-propenyl hexanoate, ethyl heptanoate, 2-propenyl heptanoate, ethyl octanoate, ethyl 2-*trans*-4-*cis*-decadienoate, methyl 2-nonyoate, benzyl propionate, benzyl isovalerate, phenylethyl isobutyrate, phenylethyl isovalerate, α,α -dimethyl phenylethyl butyrate, methyl benzoate, hexyl benzoate, benzyl benzoate, ethyl phenylacetate, geranyl phenylacetate, 1-phenylethyl phenylacetate, methyl cinnamate, benzyl cinnamate, phenylethyl cinnamate, geranyl propionate, geranyl isobutyrate, geranyl isovalerate, linalyl propionate, linalyl buryrate, linalyl isobutyrate, citronellyl propionate, citronellyl isobutyrate, citronellyl isovalerate, citronellyl tiglate, allyl 3-cyclohexylpropionate, methyl dihydrojasmonate, methyl 2-hexyl-3-oxocyclopentane-carboxylate, and mixtures thereof.

Examples of alcohols suitably released by the hydrolysis of the orthoester pro-accords are the same as those listed herein above under β -ketoesters.

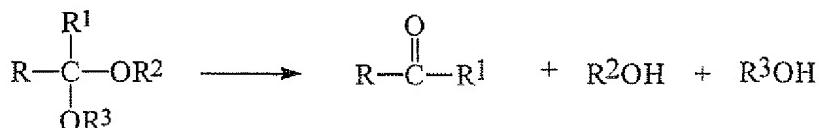
Non-limiting examples of orthoester pro-fragrances according to the present invention are tris-geranyl orthoformate, tris(*cis*-3-hexen-1-yl) orthoformate, tris(phenylethyl) orthoformate, bis(citronellyl) ethyl orthoacetate, tris(citronellyl) orthoformate, tris(*cis*-6-nonenyl) orthoformate, tris(phenoxyethyl) orthoformate, tris(geranyl, neryl) orthoformate (70:30 geranyl:neryl), tris(9-decenyl) orthoformate, tris(3-methyl-5-phenylpentanyl) orthoformate, tris(6-methylheptan-2-yl) orthoformate, tris([4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl]) orthoformate, tris[3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl] orthoformate, trismenthyl orthoformate, tris(4-isopropylcyclohexylethyl-2-yl) orthoformate, tris-(6,8-dimethylnonan-2-yl) orthoformate, tris-phenylethyl orthoacetate, tris(*cis*-3-hexen-1-yl) orthoacetate, tris(*cis*-6-nonenyl) orthoacetate, tris-citronellyl orthoacetate, bis(geranyl) benzyl orthoacetate, tris(geranyl) orthoacetate, tris(4-isopropylcyclohexylmethyl) orthoacetate, tris(benzyl) orthoacetate, tris(2,6-dimethyl-5-heptenyl) orthoacetate, bis(*cis*-3-hexen-1-yl) amyl orthoacetate, and neryl citronellyl ethyl orthobutyrate.

Acetals and ketals

A further class of compound useful as pro-accords according to the present invention are acetals and ketals having the formula:



wherein hydrolysis of the acetal or ketal releases one equivalent of aldehyde or ketone and two equivalents of alcohol according to the following scheme:



wherein R is C₁-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, preferably the moieties which substitute the aryl units are alkyl moieties, and mixtures thereof. R¹ is hydrogen, R, or in the case wherein the pro-accord is a ketal, R and R¹ can be taken together to form a ring. R² and R³ are independently selected from the group consisting of C₅-C₂₀ linear, branched, or substituted alkyl; C₄-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof.

Acetal Releasable Components: The acetals of the present invention have two types of releasable components, namely alcohols and aldehydes. Hydrolysis of an acetal will yield two equivalents of releasable alcohol and one equivalent of releasable aldehyde. The released aldehyde, when taken together with the released alcohol, forms a binary fragrance accord. For example bis(*cis*-3-hexenyl) vanillin acetal releases the binary accord vanillin/*cis*-3-hexenol.

When R¹ is hydrogen the pro-accords are capable of releasing an aldehyde component. Preferred aldehydes which are releasable components of the acetals of the present invention include but are not limited to phenylacetaldehyde, p-methyl phenylacetaldehyde, p-isopropyl phenylacetaldehyde, methylnonyl acetaldehyde, phenylpropanal, 3-(4-*t*-butylphenyl)-2-methyl propanal (Lilial), 3-(4-*t*-butylphenyl)-propanal (Bourgeonal), 3-(4-methoxyphenyl)-2-methylpropanal (Canthoxal), 3-(4-isopropylphenyl)-2-methylpropanal (Cymal), 3-(3,4-methylenedioxyphenyl)-2-methylpropanal (Helional), 3-(4-ethylphenyl)-2,2-dimethylpropanal (Floralozone), phenylbutanal, 3-methyl-5-phenylpentanal, hexanal, *trans*-2-hexenal, *cis*-hex-3-enal, heptanal, *cis*-4-heptenal, 2-ethyl-2-heptenal, 2,6-dimethyl-5-heptenal (Melonal), 2,4-heptadienal, octanal, 2-octenal, 3,7-dimethyloctanal, 3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-1,6-octadien-3-al, 3,7-dimethyl-6-octenal (citronellal), 3,7-dimethyl-7-hydroxyoctan-1-al (hydroxy citronellal), nonanal, 6-nonenal, 2,4-nonadienal, 2,6-nonadienal, decanal, 2-methyl decanal, 4-decenal, 9-decenal, 2,4-decadienal, undecanal,

2-methyldecanal, 2-methylundecanal, 2,6,10-trimethyl-9-undecenal (Adoxal), undec-10-enyl aldehyde, undec-8-enanal, dodecanal, tridecanal, tetradecanal, anisaldehyde, bourgenonal, cinnamic aldehyde, α -amylcinnam-aldehyde, α -hexyl cinnamaldehyde, methoxy-cinnamaldehyde, isocyclocitral, citronellyl oxyacet-aldehyde, cortexaldehyde, cumminic aldehyde, cyclamen aldehyde, florhydral, heliotropin, hydrotropic aldehyde, vanillin, ethyl vanillin, benzaldehyde, p-methyl benzaldehyde, 3,4-dimethoxybenzaldehyde, 3- and 4-(4-hydroxy-4-methyl-pentyl)-3-cyclohexene-1-carboxaldehyde (Lyral), 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde (Triplal), 1-methyl-3-(4-methylpentyl)-3-cyclohexencarboxaldehyde (Vernaldehyde), p-methylphenoxyacetaldehyde (Xi aldehyde), and mixtures thereof.

More preferably the aldehydes released by the acetals of the present invention are 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde (lyral), phenylacetaldehyde, methylnonyl acetaldehyde, 2-phenylpropan-1-al (hydrotropaldehyde), 3-phenylprop-2-en-1-al (cinnamaldehyde), 3-phenyl-2-pentylprop-2-en-1-al (α -amylcinnamaldehyde), 3-phenyl-2-hexylprop-2-enal (α -hexylcinnamaldehyde), 3-(4-isopropylphenyl)-2-methylpropan-1-al (cyclamen aldehyde), 3-(4-ethylphenyl)-2,2-dimethylpropan-1-al (floral ozone), 3-(4-*tert*-butylphenyl)-2-methylpropanal, 3-(3,4-methylenedioxyphenyl)-2-methylpropan-1-al (helional), 3-(4-ethylphenyl)-2,2-dimethylpropanal, 3-(3-isopropylphenyl)butan-1-al (flohydral), 2,6-dimethylhept-5-en-1-al (melonal), n-decanal, n-undecanal, n-dodecanal, 3,7-dimethyl-2,6-octadien-1-al (citral), 4-methoxybenzaldehyde (anisaldehyde), 3-methoxy-4-hydroxybenzaldehyde (vanillin), 3-ethoxy-4-hydroxybenzaldehyde (ethyl vanillin), 3,4-methylenedioxybenzaldehyde (heliotropin), 3,4-dimethoxybenzaldehyde

Ketal Releasable Components: The ketals of the present invention have two types of releasable components, namely alcohols and ketones. Hydrolysis of a ketal will yield two equivalents of releasable alcohol and one equivalent of releasable ketone. The released ketone, when taken together with the released alcohol, forms a binary fragrance accord. For example di-linalyl β -ionone ketal releases the binary accord linalool/ β -ionone.

When R¹ is a moiety as described herein above other than hydrogen, the pro-acords are capable of releasing an ketone component. Preferred ketones which are releasable components of the ketals of the present invention include but are not limited to α -damascone, β -damascone, δ -damascone, β -damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (cashmeran), *cis*-jasmone, dihydrojasmone, α -ionone, β -ionone, dihydro- β -ionone, γ -methyl ionone, α -*iso*-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)butan-2-one, methyl β -

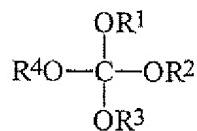
naphthal ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalid), *l*-carvone, 5-cyclohexadecen-1-one, acetophenone, decatone, 2-[2-(4-methyl-3-cyclohexenyl-1-yl)propyl]cyclopentan-2-one, 2-*sec*-butylcyclohexanone, β -dihydro ionone, allyl ionone, α -ionone, α -acetone, α -irisone, acetanisole, geranyl acetone, 1-(2-methyl-5-isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisoamylene, methyl cyclocitron, 4-*t*-pentyl cyclohexanone, p-*t*-butylcyclohexanone, o-*t*-butylcyclohexanone, ethyl amyl ketone, ethyl pentyl ketone, menthone, methyl-7,3-dihydro-2H-1,5-benzodioxepine-3-one, fenchone, and mixtures thereof.

More preferably the ketones which are released by the ketals of the present invention are α -damascone, β -damascone, δ -damascone, β -damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (cashmeran), *cis*-jasmone, dihydrojasmone, α -ionone, β -ionone, dihydro- β -ionone, γ -methyl ionone, α -iso-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)-butan-2-one, methyl β -naphthyl ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalid), *l*-carvone, 5-cyclohexadecen-1-one, and mixture thereof.

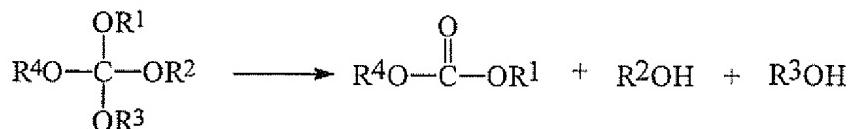
Examples of alcohols suitably released by the hydrolysis of the orthoester pro-accords are the same as those listed herein above under β -ketoesters.

Orthocarbonates

Another class of compounds useful as pro-accords according to the present invention are orthocarbonates having the formula:



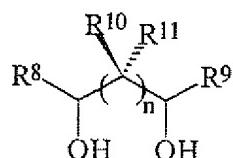
wherein hydrolysis of the orthoester releases the fragrance raw material components according to the following scheme:



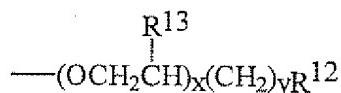
wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted

aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof. By the term "substituted" herein is meant "compatible moieties which replace a hydrogen atom". Non-limiting examples of substituents are hydroxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂H; -CO₂R'; -CONH₂; -CONHR'; -CONR'₂; wherein R' is C₁-C₁₂ linear or branched alkyl), amino, C₁-C₁₂ mono- and dialkylamino, and mixtures thereof.

In addition to the releasable alcohols listed herein above under β-ketoesters, orthocarbonates according to the present invention are also cyclic orthocarbonates which are comprised from at least one diol having the formula:



wherein R⁸, R⁹, R¹⁰, and R¹¹ are each independently hydrogen, C₁-C₂₀ linear or branched alkyl, C₁-C₂₀ linear or branched alkenyl, C₁-C₂₀ linear, branched or cyclic alkylene carboxy, C₁-C₂₀ linear, branched, or cyclic carboxyalkyl, C₁-C₂₀ linear or branched alkylene amino, C₁-C₂₀ linear or branched aminoalkyl, C₁-C₂₀ linear, branched, or cyclic alkylene carboxamido, C₁-C₂₀ linear or branched carboxamidoalkyl, alkyleneoxy having the formula:



wherein R¹² is hydrogen or methyl; R¹³ is hydrogen or C₁-C₂ alkyl; n is from 0 to 4, x is from 1 to about 20, y is from 0 to about 20.

In addition to the initial release of two equivalents of alcohol and one equivalent of carbonate by the scheme depicted herein above, the carbonate pro-fragrances which are released by the orthocarbonates can continue to hydrolyze and further release two equivalents of one or more fragrance raw material alcohol according to the following scheme:



thereby providing up to four equivalents of fragrance raw material alcohol per equivalent of delivered orthocarbonate. The carbonate pro-fragrance which is released by the

orthocarbonate may itself be a fragrance raw material in addition to being a pro-fragrance, preferably the carbonate which is released serves as a fragrance raw material. An orthocarbonate which comprises four different fragrance raw materials will always release a carbonate that is a pro-accord (hydrolyzes to release a binary accord) in addition to any further fragrance properties attributable to the carbonate.

Examples of alcohols suitably released by the hydrolysis of the orthoester pro-accords are the same as those listed herein above under β -ketoesters.

The most preferred orthocarbonate pro-accords of the present invention have each of the R¹, R², R³, and R⁴ moieties derived from a fragrance raw material alcohol, thereby the preferred pro-fragrances have a molecular weight which is at least 4 times the molecular weight of the lowest "fragrance raw material alcohol" which comprises the orthocarbonate pro-accord. Further, the preferred orthocarbonate pro-accords have a molecular weight which is greater than or equal to 350 g/mol.

Non-limiting examples of most preferred orthocarbonate pro-accords according to the present invention include: tetra-geranyl orthocarbonate, tetra-phenylethyl orthocarbonate, tetrakis(3-methyl-5-phenylpentyl) orthocarbonate, tetrakis(*cis*-3-hexenyl) orthocarbonate, bis(geranyl) bis(*cis*-3-hexenyl) orthocarbonate, bis(phenylethyl) bis(*cis*-3-hexenyl) orthocarbonate, tetrakis(citronellyl) orthocarbonate, tetrakis(linalyl) orthocarbonate, bis(linallyl) bis(geranyl) orthocarbonate, tetrakis(myrcenyl) orthocarbonate, tetrakis(cinnamyl) orthocarbonate.

According to the present invention all isomers of a fragrance raw material whether in the form of the pro-fragrance or the released fragrance raw material, are suitable for use in the present invention. When optical isomers are possible, fragrance raw materials may be included as either the separate chemical isomer or as the combined racemic mixture. For example, 3,7-dimethyl-6-octen-1-ol, commonly known by those of ordinary skill in the art as β -citronellol or cephrol, comprises a pair of optical isomers, R-(+)- β -citronellol and S-($-$)- β -citronellol. Each of these materials separately or as a racemic pair are suitable for use as fragrance raw materials in the present invention. However, those skilled in the art of fragrances, by utilization of the present invention, should not disregard the olfactory differences that individual optical isomers, admixtures of optical isomers or admixtures of positional isomers impart. By way of example, carvone, 2-methyl-5-(1-methylethenyl)-2-cyclohexene-1-one exists as two isomers; *d*-carvone and *l*-carvone. *d*-Carvone is found in oil of caraway and renders a completely different fragrance from *l*-carvone which is found in spearmint oil. According to the present invention a pro-fragrance which releases *d*-carvone will result in a different scent or fragrance than one which releases *l*-carvone. The same applies to *l*-carvone. In

addition, isomers such as *cis/trans* isomers, for example, nerol (3,7-dimethyl-*cis*-2,6-octadien-1-ol) and geraniol (3,7-dimethyl-*trans*-2,6-octadien-1-ol), are well known to those skilled in the art of perfumery and these two terpene alcohols, which commonly occur as an admixture, have different fragrance characteristics. Therefore, when formulating fragrance raw materials which comprise mixtures of isomers such as nerol/geraniol, the formulator must also take into account whether different sources of raw material have different ratios of isomers.

The formulator is not limited to the delivery of one type of fragrance, for example a top, middle, or base fragrance raw material note. Instead a mixture of top notes, a mixture of top and middle notes, or any combination of top, middle and base notes may be delivered in any suitable proportion.

As described herein above, those skilled in the art of preparing fragrance-containing compositions have categorized fragrances into three types based on their relative volatility; top, middle, and base notes. In addition, fragrances are categorized by the odor they produce; some of these descriptors are broad and others are relatively specific. For example, "floral" is a term which connotes odors associated with flowers while the term "lilac" is more specific. Descriptors used by those skilled in the art of perfumes and fragrances are *inter alia* "rose", "floral", "green", "citrus", "spicy", "honey", and "musk". The sources of these notes are not limited to one chemical class; alcohols can produce "rose", "green", and "musk" scents, while "rose" scents can comprise alcohols, ketones, terpenes, aldehydes, etc.

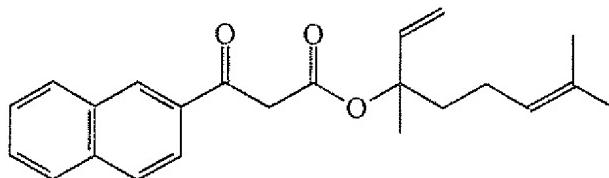
Top, middle, and base notes each serve a different purpose in the blending of fragrances and when properly formulated produce a "balanced fragrance" composition. Based on volatility, these notes are described by those skilled in the art as: the base notes having the most long lasting aroma; the middle notes, have a medium volatility; and the top notes are the most volatile. The compositions described herein below, as well as others chosen by the formulator, comprise a fragrance delivery system which utilizes the pro-fragrances of the present invention to successfully deliver a "balanced fragrance" profile.

It is also recognized by those skilled in the art that descriptors which relate to aesthetic perceptions such as "top", "middle" and "base" notes are relative terms. A fragrance raw material categorized as a top note by one formulator usually has the identical classification among most other Perfumers. The same is true for the middle and base notes, however, occasionally one formulator may classify a given fragrance raw material as a middle note rather than a top note, or vice versa, but this fact does not diminish the utility of a given compound or its absolute identity. Top, middle and base

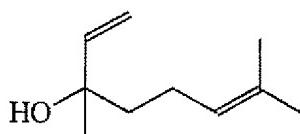
notes are now combined in a reproducible manner to produce perfumes, colognes, after-shave lotions, eau de toilettes, etc. for application to skin, which have unique and pleasant odor characteristics. Yet apart from this pleasant fragrance, a fragrance delivery system which is used to deliver a scent to a laundry detergent composition must meet a number of technical requirements. It must be sufficiently strong, it must be persistent, and it must retain its "essential character" throughout its period of evaporation and fragrance raw material release.

The compositions of the present invention comprise at least an effective amount of one or more pro-fragrances or pro-accords as described herein above. What is meant herein by "an effective amount" of a pro-accord or pro-fragrance is defined as "at least about 0.01%, preferably from about 0.01% to about 15%, more preferably from about 0.1% to about 5%, most preferably from about 0.1% to about 1% by weight, of a pro-accord as described herein above".

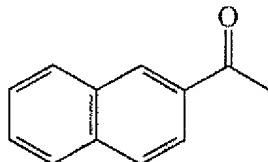
An example of a preferred pro-accord is 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-propionate having the formula:



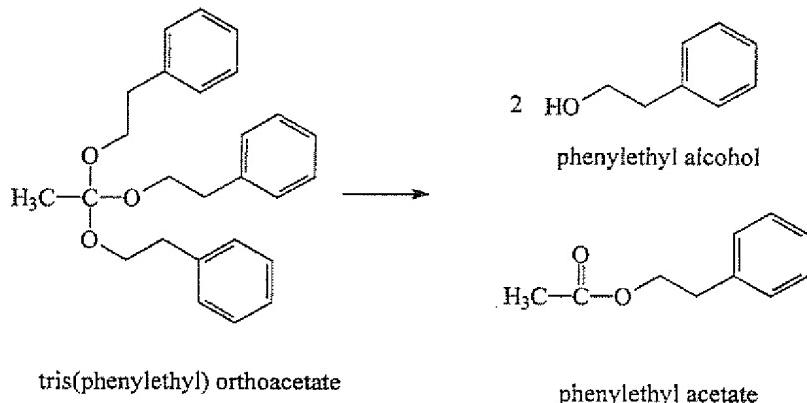
which releases at least the fragrance raw material alcohol, linalool, having the formula:



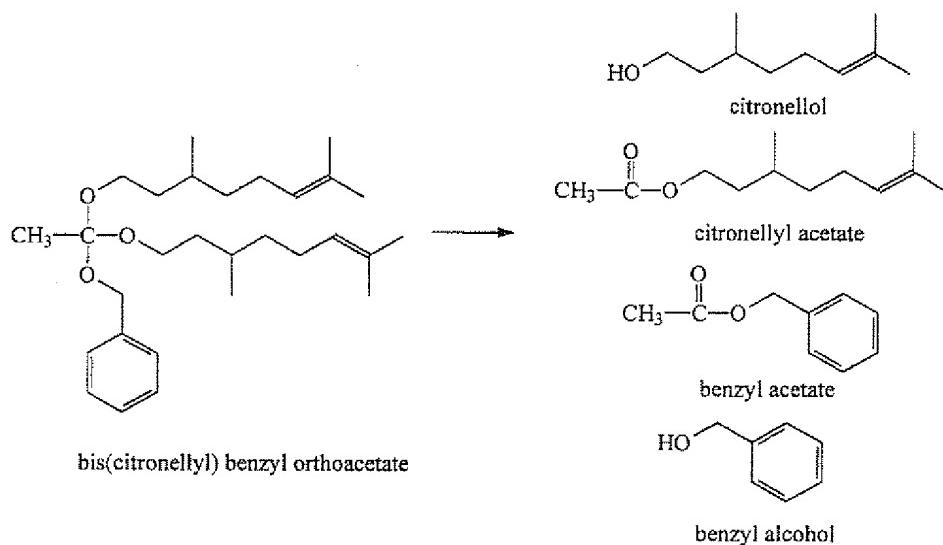
and the fragrance raw material ketone, methyl naphthyl ketone, having the formula:



A further example of a pro-accord is tris(phenylethyl) orthoacetate which releases a binary accord having a "rose" characteristic comprising 2 parts phenylethyl alcohol and 1 part phenylethyl acetate according to the following scheme:



A further example of a pro-accord is di-citronellyl benzyl acetate capable of releasing the binary fragrance accord of citronellol/citronellyl acetate having a "rose" characteristic together with the benzyl alcohol/benzyl acetate "jasmin" modifiers according to the following scheme:



The formulator may therefore deliver one fragrance or a complex accord to suitably mask the malodors which may form in the laundry detergent or fabric softener compositions.

Materials Comprising Laundry and Fabric Conditioning Compositions

Surfactant systems

The instant cleaning compositions may contain at least about 0.01 % by weight of a surfactant selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic surface active agents. Preferably the solid (i.e. granular) and

viscous semi-solid (i.e. gelatinous, pastes, etc.) systems of the present invention, surfactant is preferably present to the extent of from about 0.1% to 60 %, more preferably 0.1% to about 30% by weight of the composition.

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides are highly preferred, especially the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are described further herein and are listed in standard texts.

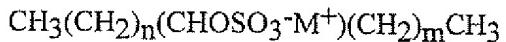
Anionic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-18 carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or

potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates (AS), such as those illustrated above, have the general formula RO_{SO3}-M⁺ wherein R is typically a linear C8-22 hydrocarbyl group and M is a water solubilizing cation. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, Eur. Pat. Appl. 439,316, Smith et al., filed January 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 17, and M is a water-solubilizing cation.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H₂SO₄ to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. See also U.S. Patent 5,349,101, Lutz et al., issued September 20, 1994; U.S. Patent 5,389,277, Prieto, issued February 14, 1995.

The preferred surfactants of the present invention are anionic surfactants, however, other surfactants useful herein are described below.

The compositions of the present invention can also comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 30%, of an nonionic detergents surfactant. Preferred nonionic surfactants such as C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C₆ to C₁₂ alkyl phenols, alkylene oxide condensates of C₈-C₂₂ alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present compositions. An extensive disclosure of these types of surfactants is found in U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975, incorporated herein by reference.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 Llenado (incorporated herein by reference) are also preferred nonionic surfactants in the compositions of the invention.

More preferred nonionic surfactants are the polyhydroxy fatty acid amides having the formula:



wherein R⁷ is C₅-C₃₁ alkyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; R⁸ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, preferably methyl or ethyl, more preferably methyl. Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyinated derivative thereof; preferred alkoxy is ethoxy or propoxy, and mixtures thereof. Preferred Q is derived from a reducing sugar in a reductive amination reaction. More preferably Q is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Q. It should be understood that it is by no means intended to exclude other suitable raw materials. Q is more preferably selected from the group consisting of -CH₂(CHOH)_nCH₂OH, -CH(CH₂OH)(CHOH)_{n-1}CH₂OH, -CH₂(CHOH)₂-(CHOR')(CHOH)CH₂OH, and alkoxyinated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide. Most preferred substituents for the Q moiety are glycityls wherein n is 4, particularly -CH₂(CHOH)₄CH₂OH.

$R^7CO-N<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

R^8 can be, for example, methyl, ethyl, propyl, isopropyl, butyl, 2-hydroxy ethyl, or 2-hydroxy propyl.

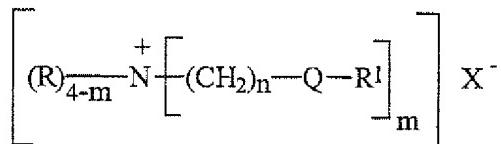
Q can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

A particularly desirable surfactant of this type for use in the compositions herein is alkyl-N-methyl glucamide, a compound of the above formula wherein R^7 is alkyl (preferably C₁₁-C₁₇), R^8 , is methyl and Q is 1-deoxyglucityl.

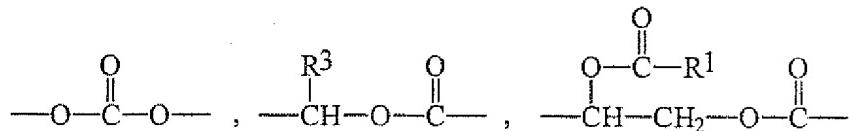
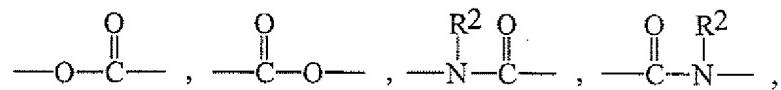
Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used.

Quaternary Ammonium Fabric Softening Active Compounds (DEQA's)

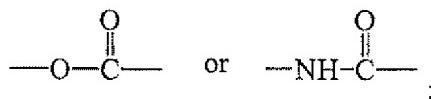
The preferred fabric softening actives according to the present invention have the formula:



wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is preferably C₁₁-C₂₂ alkyl, C₁₁-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:

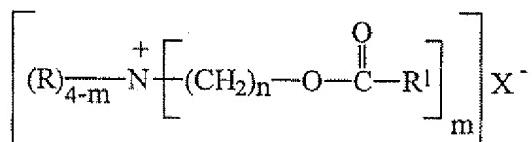


wherein R² is hydrogen, C₁-C₄ alkyl, preferably hydrogen; R³ is C₁-C₄ alkyl, preferably hydrogen or methyl; preferably Q has the formula:

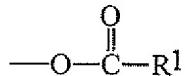


X is a softener compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and mixtures thereof, more preferably chloride and methyl sulfate. The anion can also, but less preferably, carry a double charge, in which case X⁽⁻⁾ represents half a group. The index m has a value of from 1 to 3; the index n has a value of from 1 to 4, preferably 2 or 3, more preferably 2.

More preferred softener actives according to the present invention have the formula:



wherein the unit having the formula:



is a fatty acyl moiety. Suitable fatty acyl moieties for use in the softener actives of the present invention are derived from sources of triglycerides including tallow, vegetable oils and/or partially hydrogenated vegetable oils including *inter alia* canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil.

The R¹ units are typically mixtures of linear and branched chains of both saturated and unsaturated aliphatic fatty acids, an example of which (canola oil), is described in Table I herein below.

Table I

| Fatty acyl unit | % |
|-----------------|------|
| C14 | 0.1 |
| C16 | 5.4 |
| C16:1 | 0.4 |
| C18 | 5.7 |
| C18:1 | 67.0 |
| C18:2 | 13.5 |
| C18:3 | 2.7 |

| | |
|-------|-----|
| C20 | 0.5 |
| C20:1 | 4.6 |

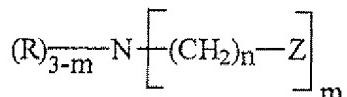
The formulator, depending upon the desired physical and performance properties of the final fabric softener active, can choose any of the above mentioned sources of fatty acyl moieties, or alternatively, the formulator can mix sources of triglyceride to form a "customized blend". However, those skilled in the art of fats and oils recognize that the fatty acyl composition may vary, as in the case of vegetable oil, from crop to crop, or from variety of vegetable oil source to variety of vegetable oil source. DEQA's which are prepared using fatty acids derived from natural sources are preferred.

A preferred embodiment of the present invention provides softener actives comprising R¹ units which have at least about 3%, preferably at least about 5%, more preferably at least about 10%, most preferably at least about 15% C₁₁-C₂₂ alkenyl, including polyalkenyl (polyunsaturated) units *inter alia* oleic, linoleic, linolenic.

For the purposes of the present invention the term "mixed chain fatty acyl units" is defined as "a mixture of fatty acyl units comprising alkyl and alkenyl chains having from 10 carbons to 22 carbon atoms including the carbonyl carbon atom, and in the case of alkenyl chains, from one to three double bonds, preferably all double bonds in the *cis* configuration". With regard to the R¹ units of the present invention, it is preferred that at least a substantial percentage of the fatty acyl groups are unsaturated, e.g., from about 25%, preferably from about 50% to about 70%, preferably to about 65%. The total level of fabric softening active containing polyunsaturated fatty acyl groups can be from about 3%, preferably from about 5%, more preferably from about 10% to about 30%, preferably to about 25%, more preferably to about 18%. As stated herein above *cis* and *trans* isomers can be used, preferably with a *cis/trans* ratio is of from 1:1, preferably at least 3:1, and more preferably from about 4:1 to about 50:1, more preferably about 20:1, however, the minimum being 1:1.

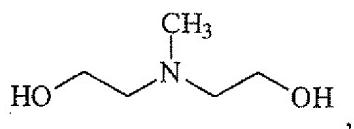
The R¹ units suitable for use in the present invention can be further characterized by the Iodine Value (IV) of the parent fatty acid, said IV is preferably from about 20, more preferably from about 50, most preferably from about 70, to a value of about 140, preferably to about 130, more preferably to about 115. However, formulators, depending upon which embodiment of the present invention they choose to execute, may wish to add an amount of fatty acyl units which have Iodine Values outside the range listed herein above. For example, "hardened stock" (IV less than or equal to about 10) may be combined with the source of fatty acid admixture to adjust the properties of the final softener active. A further preferred embodiment of the present invention comprises DEQA's wherein the average Iodine Value for R¹ is approximately 45.

Amines which are used to prepare the preferred fabric softening actives of the present invention have the formula:

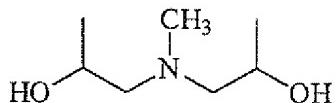


wherein R is the same as defined herein above; each Z is independently selected from the group consisting of -OH, -CHR³OH, -CH(OH)CH₂OH, -NH₂, and mixtures thereof; preferably -OH, -NH₂, and mixtures thereof; R³ is C₁-C₄ alkyl, preferably methyl; the indices m and n are the same as defined hereinabove.

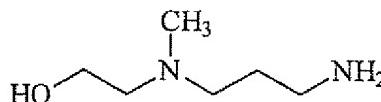
Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:



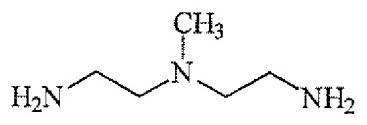
methyl bis(2-hydroxypropyl)amine having the formula:



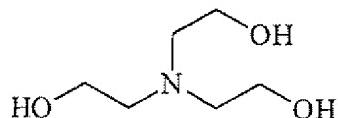
methyl (3-aminopropyl) (2-hydroxyethyl)amine having the formula:



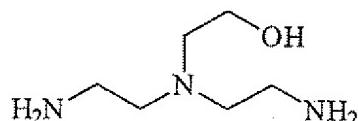
methyl bis(2-aminoethyl)amine having the formula:



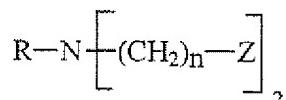
triethanol amine having the formula:



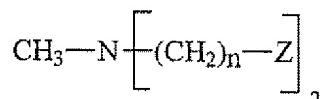
bis(2-aminoethyl) ethanolamine having the formula:



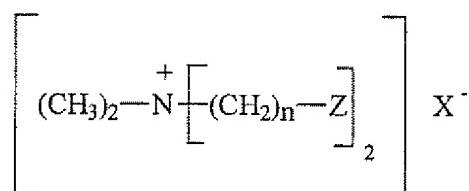
For the purposes of the present invention, R moieties which are introduced during the quaternization step are preferably methyl. In the case of amines having the formula:



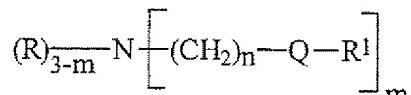
R is preferably the same moiety (i.e. methyl) which is introduced during the quaternization step. For example, a methyl amine having the formula:



is preferably quaternized to the softener active having the general formula:

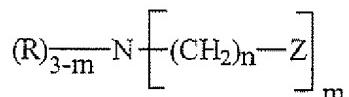


In one embodiment of the present invention, the fabric softening active precursor amine mixture is not fully quaternized, that is, some free amine having the general formula:



is still present in the final fabric softener mixture.

A yet further embodiment of the present invention comprises an amine of the formula:



wherein not all of the Z units are fully reacted with a fatty acyl moiety thereby leaving an amount of amine and/or quaternized ammonium compound in the final fabric softener active admixture having one or more Z units unreacted and thereby not transformed into an ester or amide..

The following are examples of preferred softener actives according to the present invention.

N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 N,N-di(canolyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
 N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
 N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 N-(2-canolyloxy-2-ethyl)-N-(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
 N,N,N-tri(canolyl-oxy-ethyl)-N-methyl ammonium chloride;
 N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
 N-(2-canolyloxy-2-oxoethyl)-N-(canolyl)-N,N-dimethyl ammonium chloride;
 1,2-ditallowyloxy-3-N,N,N-trimethylammoniopropane chloride; and
 1,2-dicanolyloxy-3-N,N,N-trimethylammoniopropane chloride;
 and mixtures of the above actives.

Particularly preferred is N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated and N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride.

The amount of fabric softening active present in the compositions of the present invention is at least about 2%, preferably from about 2%, more preferably from about 5% to about 60%, more preferably to about 40% by weight, of the composition.

ADJUNCT INGREDIENTS

The following are non-limiting examples of adjunct ingredients useful in the laundry compositions of the present invention, said adjunct ingredients include builders, optical brighteners, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

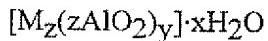
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred

layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

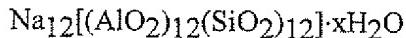
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the

composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

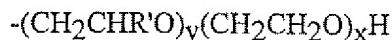
In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Dispersants

The compositions of the present invention may also optionally comprise at least about 0.1% by weight, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight, of a water-soluble substituted or unsubstituted, modified or unmodified polyalkyleneimine dispersant, said dispersant comprises a polyamine backbone, preferably said backbone having a molecular weight of from about 100 to about 3000 daltons having the formula:



wherein R is preferably C₂-C₆ alkylene, m is from about 3 to 70, n is from 0 to about 35, one or more of the polyamine backbone N-H unit hydrogens are "substituted", that is replaced with a substituent which increases the hydrophobic or hydrophilic dispersancy of said polyamine, preferably one or more backbone hydrogens, more preferably all hydrogens are replaced by an propyleneoxy/ethyleneoxy unit having the formula:



wherein R' is methyl or ethyl, x and y are preferably from about 0 to about 50, provided x + y is at least 1; and wherein further each nitrogen which comprises the polyalkyleneimine backbone may be optionally "modified" by quaternization or by oxidation to the N-oxide.

A further description of polyalkyleneimine dispersants is found in U.S. 4,597,898, VanderMeer, issued July 1, 1986; European Patent Application 111,965, Oh and Gosselink, published June 27, 1984; European Patent Application 111,984, Gosselink, published June 27, 1984; European Patent Application 112,592, Gosselink, published July 4, 1984; U.S. 4,548,744, Connor, issued October 22, 1985; and U.S.

5,565,145 Watson et al., issued October 15, 1996; all of which are included herein by reference. However, any suitable clay/soil dispersent or anti-redeposition agent can be used in the laundry compositions of the present invention.

Soil Release Agents

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*.

Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

Solvents and Carrier

The fabric softener compositions of the present invention may be liquid in form and, therefore be formulated into an aqueous system or optionally be formulated with a solvent-water system as the liquid carrier. For the liquid fabric softeners of the present invention containing solvents, the solvent preferably comprises less than about 40%, preferably from about 10% to about 35%, more preferably from about 12% to about 25%, and even more preferably from about 14% to about 20%, by weight of the composition. The solvent is selected to minimize solvent odor impact in the composition and to provide a low viscosity to the final composition. For example, isopropyl alcohol is not very effective and has a strong odor. n-Propyl alcohol is more effective, but also has a distinct odor. Several butyl alcohols also have odors but can be used for effective clarity/stability, especially when used as part of a solvent system to minimize their odor. The alcohols are also selected for optimum low temperature stability, that is they are able to form compositions that are liquid with acceptable low viscosities and translucent, preferably clear, down to about 40°F (about 4.4°C) and are able to recover after storage down to about 20°F (about 6.7°C).

The suitability of any solvent for the formulation of the liquid, concentrated, preferably clear, fabric softener compositions herein with the requisite stability is surprisingly selective. Suitable solvents can be selected based upon their octanol/water partition coefficient (P). Octanol/water partition coefficient of a solvent is the ratio between its equilibrium concentration in octanol and in water. The partition coefficients of the solvent ingredients of this invention are conveniently given in the form of their logarithm to the base 10, logP.

The logP of many ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in *Comprehensive Medicinal Chemistry*, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. These ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are preferably used instead of the experimental logP values in the selection of the solvent ingredients which are useful in the present invention. Other

methods that can be used to compute ClogP include, e.g., Crippen's fragmentation method as disclosed in J. Chem. Inf. Comput. Sci., 27, 21 (1987); Viswanadhan's fragmentation method as disclosed in J. Chem. Inf. Comput. Sci., 29, 163 (1989); and Broto's method as disclosed in Eur. J. Med. Chem. - Chim. Theor., 19, 71 (1984).

The solvents herein are selected from those having a ClogP of from about 0.15 to about 0.64, preferably from about 0.25 to about 0.62, and more preferably from about 0.40 to about 0.60, said solvent preferably being at least somewhat asymmetric, and preferably having a melting, or solidification, point that allows it to be liquid at, or near room temperature. Solvents that have a low molecular weight and are biodegradable are also desirable for some purposes. The more asymmetric solvents appear to be very desirable, whereas the highly symmetrical solvents such as 1,7-heptanediol, or 1,4-bis(hydroxymethyl) cyclohexane, which have a center of symmetry, appear to be unable to provide the essential clear compositions when used alone, even though their ClogP values fall in the preferred range.

Operable solvents are disclosed and listed below which have ClogP values which fall within the requisite range. These include mono-ols, C6 diols, C7 diols, octanediol isomers, butanediol derivatives, trimethylpentanediol isomers, ethylmethylpentanediol isomers, propyl pentanediol isomers, dimethylhexanediol isomers, ethylhexanediol isomers, methylheptanediol isomers, octanediol isomers, nonanediol isomers, alkyl glycercyl ethers, di(hydroxy alkyl) ethers, and aryl glycercyl ethers, aromatic glycercyl ethers, alicyclic diols and derivatives, C₃C₇ diol alkoxylated derivatives, aromatic diols, and unsaturated diols. Particularly preferred solvents include hexanediols such as 1,2-Hexanediol and 2-Ethyl-1,3-hexanediol and pentanediols such as 2,2,4-Trimethyl-1,3-pentanediol.

Perfumes

The products herein can also contain from about 0.1% to about 60%, preferably from about 1% to about 50%, cyclodextrin/perfume inclusion complexes and/or free perfume, as disclosed in U.S. Pat. Nos. 5,139,687, Borcher et al., issued Aug. 18, 1992; and 5,234,610, Gardlik et al., to issue Aug. 10, 1993, which are incorporated herein by reference. Perfumes are highly desirable, can usually benefit from protection, and can be complexed with cyclodextrin. Fabric softening products typically contain perfume to provide an olfactory aesthetic benefit and/or to serve as a signal that the product is effective.

The optional perfume ingredients and compositions of this invention are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations. Suitable perfume compounds and

compositions can be found in the art including U.S. Pat. Nos.: 4,145,184, Brain and Cummins, issued Mar. 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference. Many of the art recognized perfume compositions are relatively substantive to maximize their odor effect on substrates. However, it is a special advantage of perfume delivery via the perfume/cyclodextrin complexes that nonsubstantive perfumes are also effective.

If a product contains both free and complexed perfume, the escaped perfume from the complex contributes to the overall perfume odor intensity, giving rise to a longer lasting perfume odor impression.

As disclosed in U.S. Pat. No. 5,234,610, Gardlik/Trinh/Banks/Benvegnu, issued Aug. 3, 1993, said patent being incorporated herein by reference, by adjusting the levels of free perfume and perfume/CD complex it is possible to provide a wide range of unique perfume profiles in terms of timing (release) and/or perfume identity (character). Solid, dryer-activated fabric conditioning compositions are a uniquely desirable way to apply the cyclodextrins, since they are applied at the very end of a fabric treatment regimen when the fabric is clean and when there are almost no additional treatments that can remove the cyclodextrin.

Stabilizers

Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA;

long chain esters (C₈-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from Monsanto with a chemical name of 1-hydroxyethylidene-1, 1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene-sulfonic acid/sodium salt, EDDS, and DTPA®, available from Aldrich with a chemical name of diethylenetriaminepentaacetic acid.

Concentration aids

Concentrated compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. Surfactant concentration aids are typically selected from the group consisting of single long chain alkyl cationic surfactants; nonionic surfactants; amine oxides; fatty acids; or mixtures thereof, typically used at a level of from 0 to about 15% of the composition.

Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

Other Adjunct Ingredients

The present invention can include other adjunct components (minor components) conventionally used in textile treatment compositions, for example, colorants, preservatives, optical brighteners, opacifiers, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, and the like.

For examples of other suitable ingredients useful in fabric softener containing compositions see WO 97/03169 included herein by reference.

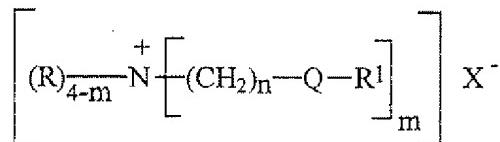
METHOD OF USE

The present invention to methods for providing a laundry detergent composition having reduced malodor, comprising the step of adding a effective amount of a pro-accord to a laundry detergent composition comprising:

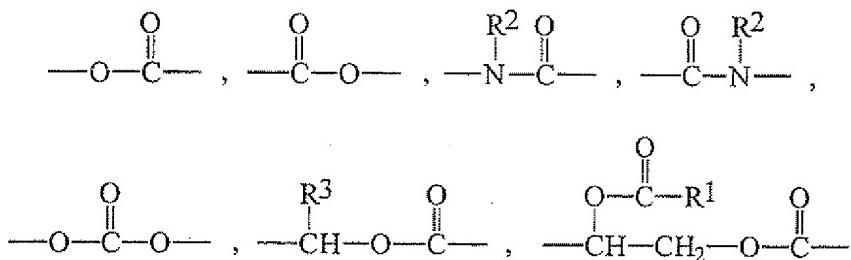
- a) at least about 0.01% by weight, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a detergents surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant;
- b) the balance carriers and adjunct ingredients, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

The present invention also relates to methods for providing a fabric softener composition having reduced malodor, comprising the step of adding a effective amount of a pro-accord to a fabric softener composition comprising:

- a) at least about 2%, preferably from about 2%, more preferably from about 3% to about 60%, more preferably to about 40% by weight, of a fabric softening active having the formula:



wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:



wherein R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; R³ is hydrogen, C₁-C₄ alkyl, and mixtures thereof; X is a softener compatible anion; m is from 1 to 3; n is from 1 to 4; and

- b) the balance carriers and adjunct ingredients, said adjunct ingredients selected from the group consisting of nonionic fabric softening agents, concentration aid, soil release agent, perfume, preservatives, stabilizers, colorants, optical brighteners, opacifiers, fabric conditioning agents, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, cationic charge boosters, and mixtures thereof.

What is meant herein by "an effective amount" of a pro-accord or pro-fragrance is defined as "at least about 0.01%, preferably from about 0.01% to about 15%, more preferably from about 0.1% to about 5%, most preferably from about 0.1% to about 1% by weight, of a pro-accord as described herein above".

The method of the present invention can be conducted in any manner suitable to the formulator. For example, the fragrance releasing pro-accord material may be added at any step during formulation of the laundry detergent or fabric softening composition, provided that the final form of the composition allows for adequate delivery of the released fragrance.

EXAMPLE 1

Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate

A mixture of linalool (100 g, 0.648 mol) and 4-dimethylaminopyridine (0.40 g, 3.20 mmol) in a 500 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer is heated to 55 °C. Diketene (54.50 g, 0.648 mol) is added dropwise in the course of 30 min. The mixture has a slight exotherm and turns from yellow to red during this time. After stirring an additional hour at 50 °C, the mixture is cooled to room temperature. At this point, NMR analysis indicates the reaction is complete. The material from this lot is carried onto the next step. Purification of an earlier sample from this route by flash chromatography

(elution with dichloromethane) yields the desired product in 92% yield and nearly colorless.

EXAMPLE 2

Preparation of 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate

A mixture of dihydromyrcenol (37.88 g, 0.240 mol) and 4-dimethylaminopyridine (0.16 g, 1.30 mmol) in a 100 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer is heated to 50-60 °C. Diketene (20.16 g, 0.240 mol) is added dropwise in the course of 15 min. The mixture has a slight exotherm and turned from yellow to red during this time. After stirring an additional hour at 50 °C, the mixture is cooled to room temperature. At this point, NMR analysis indicates the reaction is complete. Purification of the product mixture by flash chromatography (elution with dichloromethane) yields the desired product in 95% yield as a nearly colorless oil.

EXAMPLE 3

Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate

Crude 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate (154.51, 0.648 mol) from above is placed in a 3000 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer. The contents are dissolved in 350 mL of dichloromethane and treated with powdered calcium hydroxide (50.44 g, 0.681 mol). The mixture is stirred at 30 °C for 30 min and then heated to 40 °C. 2-Naphthoyl chloride (142.12 g, 0.746 mol) dissolved in 20 mL of dichloromethane is added dropwise over 15 min. The mixture continues to be heated at this temperature for 1 h. Ammonium chloride (36.41 g, 0.681 mol) dissolved in 250 mL of water is added to the reaction mixture and the pH adjusted to ~9 with 28% ammonium hydroxide. After stirring 30 min at 35 °C the pH is adjusted to ~1 with 20% HCl. The mixture is transferred to a separatory funnel containing diethyl ether (500 mL) and water (500 mL). The layers are separated and the organic phase is washed with saturated NaHCO₃ solution (2 x 500 mL), dried over MgSO₄, filtered and concentrated by rotary evaporation to give a yellow red oil. At this point a light yellow solid precipitates from the mixture. An equal volume of hexane is added and the solids is collected by filtration and dried. NMR analysis indicates the solid is 2-naphthoic acid. The eluent is concentrated again by rotary evaporation to give a red oil. The oil is taken up in an equal volume of dichloromethane, passed through a plug of silica gel (400 g) and eluted with dichloromethane. The mixture is concentrated by rotary evaporation and stripped by Kugelrohr distillation (40 °C, 0.10 mm Hg, 30 min) to yield 173.26 g (76.3%) of the product as a red oil; this product is a mixture of a 1:10 molar ratio of linalyl acetoacetate

to linalyl (2-naphthoyl)acetate. A portion of this material is purified by column chromatography (elution with 2.5% ethyl acetate in hexanes) to give the desired product as a light yellow oil.

The following are examples of granular detergent compositions comprising the fragrance delivery system of the present invention.

TABLE I

| <u>Ingredient</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> | <u>weight %</u> |
|--|----------|----------|----------|----------|-----------------|
| Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate | 13.3 | 13.7 | 10.4 | 11.1 | |
| Sodium C ₁₄ -C ₁₅ alcohol sulfate | 3.9 | 4.0 | 4.5 | 11.2 | |
| Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (0.5) sulfate | 2.0 | 2.0 | 0.0 | 0.0 | |
| Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (6.5) | 0.5 | 0.5 | 0.5 | 1.0 | |
| Tallow fatty acid | 0.0 | 0.0 | 0.0 | 1.1 | |
| Sodium tripolyphosphate | 0.0 | 41.0 | 0.0 | 0.0 | |
| Zeolite A, hydrate (0.1-10 micron size) | 26.3 | 0.0 | 21.3 | 28.0 | |
| Sodium carbonate | 23.9 | 12.4 | 25.2 | 16.1 | |
| Sodium Polyacrylate (45%) | 3.4 | 0.0 | 2.7 | 3.4 | |
| Sodium silicate (1:6 ratio NaO/SiO ₂)(46%) | 2.4 | 6.4 | 2.1 | 2.6 | |
| Sodium sulfate | 10.5 | 10.9 | 8.2 | 15.0 | |
| Sodium perborate | 1.0 | 1.0 | 5.0 | 0.0 | |
| Poly(ethyleneglycol), MW ~4000 (50%) | 1.7 | 0.4 | 1.0 | 1.1 | |
| Citric acid | 0.0 | 0.0 | 3.0 | 0.0 | |
| Nonyl ester of sodium p-hydroxybenzene-sulfonate | 0.0 | 0.0 | 5.9 | 0.0 | |
| Soil release polymer ¹ | 1.5 | 1.5 | 1.5 | 1.5 | |
| Pro-accord ² | 1.0 | 1.5 | 0.0 | 0.0 | |
| Pro-accord ³ | 0.0 | 0.0 | 2.5 | 1.5 | |
| Minors ⁴ | 7.0 | 2.1 | 4.1 | 6.3 | |

1. Soil release polymer according to U.S. Patent 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995.
2. Pro-accord according to Example 1.
3. Pro-accord according to Example 3.
4. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, protease, lipase, cellulase, chelating agents, dye

transfer inhibiting agents, additional water, and fillers, including CaCO₃, talc, silicates, etc.

The following illustrate liquid laundry detergent compositions comprising the fragrance delivery system according to the present invention.

TABLE II

| Ingredients | Weight % | | | | |
|---|----------|---------|---------|---------|---------|
| | 8 | 9 | 10 | 11 | 12 |
| Polyhydroxy coco-fatty acid amide | 3.50 | 3.50 | 3.15 | 3.50 | 3.00 |
| NEODOL 23-9 ¹ | 2.00 | 0.60 | 2.00 | 0.60 | 0.60 |
| C ₂₅ Alkyl ethoxylate sulphate | 19.00 | 19.40 | 19.00 | 17.40 | 14.00 |
| C ₂₅ Alkyl sulfate | -- | -- | -- | 2.85 | 2.30 |
| C ₁₀ -Aminopropylamide | -- | -- | -- | 0.75 | 0.50 |
| Citric acid | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Tallow fatty acid | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Ethanol | 3.41 | 3.47 | 3.34 | 3.59 | 2.93 |
| Propanediol | 6.22 | 6.35 | 6.21 | 6.56 | 5.75 |
| Monomethanol amine | 1.00 | 0.50 | 0.50 | 0.50 | 0.50 |
| Sodium hydroxide | 3.05 | 2.40 | 2.40 | 2.40 | 2.40 |
| Sodium p-toluene sulfonate | 2.50 | 2.25 | 2.25 | 2.25 | 2.25 |
| Borax | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Protease ² | 0.88 | 0.88 | 0.88 | 0.88 | 0.88 |
| Lipolase ³ | 0.04 | 0.12 | 0.12 | 0.12 | 0.12 |
| Duramyl ⁴ | 0.10 | 0.10 | 0.10 | 0.10 | 0.40 |
| CAREZYME | 0.053 | 0.053 | 0.053 | 0.053 | 0.053 |
| Optical Brightener | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| Pro-accord ⁵ | 1.18 | 1.18 | 1.18 | 1.18 | 1.75 |
| Soil release agent ⁶ | 0.22 | 0.15 | 0.15 | 0.15 | 0.15 |
| Fumed silica | 0.119 | 0.119 | 0.119 | 0.119 | 0.119 |
| Minors, aesthetics, water | balance | balance | balance | balance | balance |

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
4. Disclosed in WO 9510603 A and available from Novo.

5. Pro-accord according to Example 3.
6. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel *et al.*, issued November 6, 1990.

TABLE III

weight %

| Ingredients | 13 | 14 | 15 |
|---|---------|---------|---------|
| DEQA ¹ (85% active in ethanol) | 19.9 | -- | 15.3 |
| DEQA ² (85% active in ethanol) | -- | 19.9 | -- |
| DEQA ³ (85% active in ethanol) | 10.7 | 10.7 | 15.3 |
| Ethanol | -- | -- | 2 |
| Irganox® 3125 | 0.01 | 0.01 | 0.02 |
| DTPA | 0.01 | 0.01 | 0.01 |
| 1,2-Hexanediol | 18 | 18 | 18 |
| Pro-accord ⁴ | 2.2 | 3.2 | 1.8 |
| HCl (pH 2.5-4.0) | 0.005 | 0.005 | 0.005 |
| Distilled Water | balance | balance | balance |

1. N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated.
2. N,N-di(canoloyl-oxy-ethyl)-N,N-dimethyl ammonium chloride.
3. N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride.
4. Pro-accord according to Example 3.

TABLE IV

weight %

| Ingredients | 16 | 17 | 18 |
|---|---------|---------|---------|
| DEQA ¹ (85% active in ethanol) | -- | 32.5 | -- |
| DEQA ² (85% active in ethanol) | 15.3 | -- | 32.5 |
| DEQA ³ (85% active in ethanol) | 15.3 | 17.5 | 17.5 |
| Ethanol | 2 | 2 | 2 |
| Irganox® 3125 | 0.02 | 0.03 | 0.03 |
| DTPA | 0.1 | 0.1 | 0.1 |
| 1,2-Hexanediol | 18 | 28 | 28 |
| Pro-accord ⁴ | 1.35 | 1.3 | 1.3 |
| HCl (pH 2.5-4.0) | 0.005 | 0.005 | 0.005 |
| Distilled Water | balance | balance | balance |

1. N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated.
2. N,N-di(canoloyl-oxy-ethyl)-N,N-dimethyl ammonium chloride.
3. N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride.
4. Pro-accord according to Example 1.

TABLE V

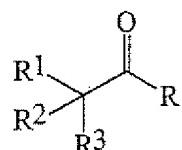
weight %

| Ingredients | 19 | 20 | 21 |
|---|---------|---------|---------|
| DEQA ¹ (85% active in ethanol/hexylene glycol) | 30.6 | 30.6 | -- |
| DEQA ² (85% active in ethanol/hexylene glycol 1:1) | -- | -- | 30.6 |
| 2,2,4-Trimethylpentane-1,3-diol | 15.0 | -- | 12.0 |
| Irganox® 3125 | 0.01 | 0.01 | 0.01 |
| DTPA | 0.01 | 0.01 | 0.01 |
| 2-Ethyl-1,3-hexanediol | -- | 15.0 | -- |
| 1,4-Cyclohexanedimethanol | 5.0 | 5.0 | 5.0 |
| Pro-accord ³ | 2.5 | 2.5 | 2.5 |
| HCl (pH 2.5-4.0) | 0.005 | 0.005 | 0.005 |
| Distilled Water | balance | balance | balance |

1. N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated.
2. N,N-di(canoloyl-oxy-ethyl)-N,N-dimethyl ammonium chloride.
3. Tris(citronellyl) orthoformate.

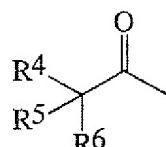
What is claimed is:

1. A method for providing a laundry detergent composition having reduced malodor, comprising the step of adding an effective amount of one or more pro-accords to a laundry detergent composition comprising:
 - a) at least 0.01% by weight, preferably from 0.1% to 60%, more preferably from 0.1% to 30% by weight, of a detergentsurfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant;
 - b) the balance carriers and adjunct ingredients, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.
2. A method according to Claim 1 wherein said pro-accord is selected from the group consisting of:
 - i) a b-ketoester having the formula:



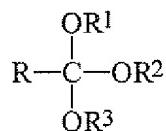
wherein R is alkoxy derived from a fragrance raw material alcohol; R¹, R², and R³ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or

unsubstituted alkylenearyl, C₆-C₃₀ substituted or unsubstituted aryl, C₂-C₂₀ substituted or unsubstituted alkyleneoxy, C₃-C₂₀ substituted or unsubstituted alkyleneoxyalkyl, C₇-C₂₀ substituted or unsubstituted alkylenearyl, C₆-C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R¹, R², or R³ is a unit having the formula:



wherein R⁴, R⁵, and R⁶ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₁-C₃₀ substituted or unsubstituted linear alkoxy, C₃-C₃₀ substituted or unsubstituted branched alkoxy, C₃-C₃₀ substituted or unsubstituted cyclic alkoxy, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkylenearyl; or R⁴, R⁵, and R⁶ can be taken together to form C₆-C₃₀ substituted or unsubstituted aryl; and mixtures thereof;

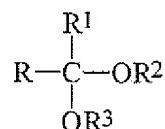
ii) an orthoester having the formula:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-

C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof;

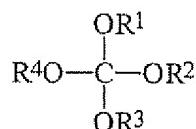
- iii) an acetal or a ketal having the formula:



wherein R is C₃-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof;

R¹ is hydrogen or R; R² and R³ are each independently selected from the group consisting of C₅-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ substituted aryl, and mixtures thereof;

- iv) an orthocarbonate having the formula:



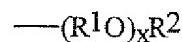
wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof; and

- v) mixtures thereof.

3. A method according to either Claim 1 or 2 wherein said composition comprises at least 0.01%, preferably from 0.01% to 15%, more preferably from 0.1% to 5%, most preferably from 0.1% to 1% by weight, of said pro-accord.
4. A method according to any of Claims 1-3 wherein said composition comprises at least 0.1%, preferably from 0.2% to 10%, more preferably from 0.5% to 5% by weight, of a polyalkyleneimine soil dispersant, said dispersant comprising a backbone having the formula:

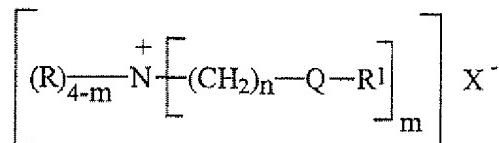


wherein R is C₂-C₆ alkylene, m is from 3 to 70, n is from 0 to 35; wherein each hydrogen atom of said backbone is optionally substituted by an alkyleneoxy unit having the formula:

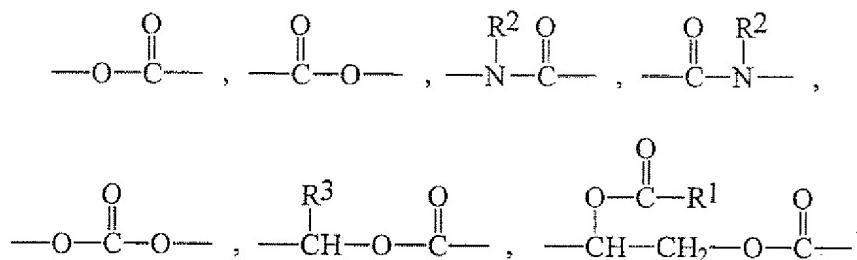


wherein R¹ is C₂-C₄ linear or branched alkylene, R² is hydrogen, C₁-C₄ alkyl, and mixtures thereof; x is from 1 to 50.

5. A method for providing a fabric softener composition having reduced malodor, comprising the step of adding an effective amount of a pro-accord to a fabric softener composition comprising:
 - a) at least 2%, preferably from 2% to 60%, more preferably to 40% by weight, of a fabric softening active having the formula:

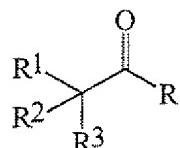


wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:



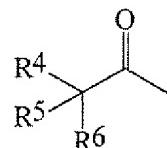
wherein R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; R³ is hydrogen, C₁-C₄ alkyl, and mixtures thereof; X is a softener compatible anion; m is from 1 to 3; n is from 1 to 4; and

- b) the balance carriers and adjunct ingredients, said adjunct ingredients selected from the group consisting of nonionic fabric softening agents, concentration aid, soil release agent, perfume, preservatives, stabilizers, colorants, optical brighteners, opacifiers, fabric conditioning agents, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, cationic charge boosters, and mixtures thereof.
6. A method according to Claim 5 wherein said pro-accord is selected from the group consisting of:
- i) a b-ketoester having the formula:



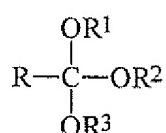
wherein R is alkoxy derived from a fragrance raw material alcohol; R¹, R², and R³ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkylyl, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted aryl, C₂-C₂₀ substituted or unsubstituted alkylenearyl, C₆-C₃₀ substituted or unsubstituted aryl, C₂-C₂₀ substituted or unsubstituted alkyleneoxy, C₃-C₂₀ substituted or

unsubstituted alkyleneoxyalkyl, C₇-C₂₀ substituted or unsubstituted alkylenearyl, C₆-C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R¹, R², or R³ is a unit having the formula:



wherein R⁴, R⁵, and R⁶ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₁-C₃₀ substituted or unsubstituted linear alkoxy, C₃-C₃₀ substituted or unsubstituted branched alkoxy, C₃-C₃₀ substituted or unsubstituted cyclic alkoxy, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkylenearyl; or R⁴, R⁵, and R⁶ can be taken together to form C₆-C₃₀ substituted or unsubstituted aryl; and mixtures thereof;

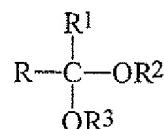
- ii) an orthoester having the formula:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy;

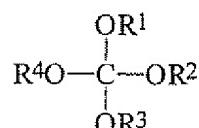
C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof;

- iii) an acetal or a ketal having the formula:



wherein R is C₃-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹ is hydrogen or R; R² and R³ are each independently selected from the group consisting of C₅-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ substituted aryl, and mixtures thereof;

- iv) an orthocarbonate having the formula:

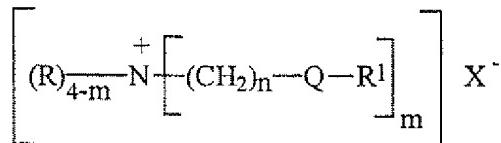


wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof; and

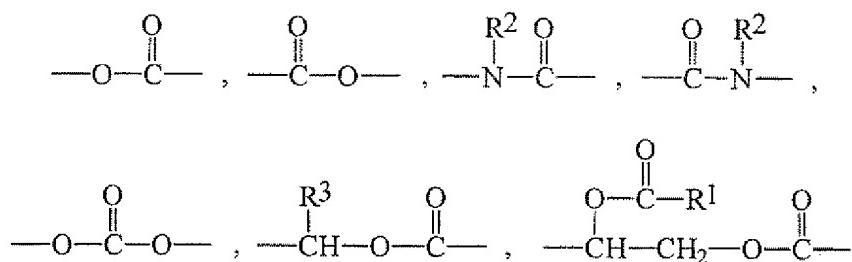
- v) mixtures thereof.

- 7. A method according to either Claim 5 or 6 wherein said composition comprises at least 0.01%, preferably from 0.01% to 15%, more preferably from 0.1% to 5%, most preferably from 0.1% to 1% by weight, of said pro-accord.

8. A method according to any of Claims 5-7 wherein said composition further comprises a solvent having a ClogP of from 0.15 to 0.64.
9. A laundry detergent composition having reduced malodor, comprising:
 - a) an effective amount of a pro-accord;
 - b) at least 0.01% by weight, preferably from 0.1% to 60%, more preferably from 0.1% to 30% by weight, of a deterotive surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant;
 - c) the balance carriers and adjunct ingredients, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.
10. A fabric softener composition having reduced malodor, comprising:
 - a) an effective amount of a pro-accord;
 - b) at least 2%, preferably from 2%, more preferably from 3% to 60%, more preferably to 40% by weight, of a fabric softening active having the formula:



wherein each R is independently C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; R¹ is C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, and mixtures thereof; Q is a carbonyl moiety having the formula:



wherein R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; R³ is hydrogen, C₁-C₄ alkyl, and mixtures thereof; X is a softener compatible anion; m is from 1 to 3; n is from 1 to 4; and

- c) the balance carriers and adjunct ingredients, said adjunct ingredients selected from the group consisting of nonionic fabric softening agents, concentration aid, soil release agent, perfume, preservatives, stabilizers, colorants, optical brighteners, opacifiers, fabric conditioning agents, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, spotting agents, germicides, fungicides, anti-corrosion agents, antifoam agents, cationic charge boosters, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01632

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/50 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ^a | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------------------|--|-----------------------|
| X | WO 97 34989 A (PROCTER & GAMBLE) 25 September 1997 see claims; examples 3,4,7 ---- | 1-3,9 |
| P,X | EP 0 864 642 A (PROCTER & GAMBLE) 16 September 1998 see claims; examples ---- | 1,3-5,7, 9,10 |
| X | WO 97 16523 A (PROCTER & GAMBLE) 9 May 1997 see claims; examples 9,10 ---- | 1,3,5,9, 10 |
| A | WO 97 06235 A (PROCTER & GAMBLE) 20 February 1997 see page 1, line 5 - line 11; claim 1 ---- | 1,3,9 -/- |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

^a Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

| | |
|---|--|
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 6 January 1999 | 02/02/1999 |

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

| | |
|-----------------|-----------------|
| Interr. | Application No. |
| PCT/IB 98/01632 | |

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | DATABASE WPI Section Ch, Week 8951 Derwent Publications Ltd., London, GB; Class A97, AN 89-372973 XP002023917 & JP 01 256597 A (KAO CORP) , 13 October 1989 see abstract ---- | 1-3,9 |
| A | US 4 915 866 A (MOOKHERJEE BRAJA D ET AL) 10 April 1990 see claim 1 ---- | 1,3,9 |
| A | DATABASE WPI Section Ch, Week 9232 Derwent Publications Ltd., London, GB; Class D21, AN 92-265722 XP002089225 & JP 04 183797 A (AJINOMOTO KK) , 30 June 1992 see abstract ---- | 1,3,9 |
| A | DATABASE WPI Section Ch, Week 8915 Derwent Publications Ltd., London, GB; Class D23, AN 89-110714 XP002089226 & JP 01 056798 A (TAIYO KORYO KK) , 3 March 1989 see abstract ---- | 1-3,9 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/IB 98/01632

| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
|--|---|------------------|-------------------------|-----------|------------------|
| WO 9734989 | A | 25-09-1997 | WO | 9734986 A | 25-09-1997 |
| | | | AU | 2432197 A | 10-10-1997 |
| | | | AU | 2432297 A | 10-10-1997 |
| | | | AU | 5372096 A | 10-10-1997 |
| | | | WO | 9734578 A | 25-09-1997 |
| EP 0864642 | A | 16-09-1998 | WO | 9841605 A | 24-09-1998 |
| WO 9716523 | A | 09-05-1997 | US | 5721202 A | 24-02-1998 |
| | | | CA | 2236658 A | 09-05-1997 |
| | | | EP | 0876467 A | 11-11-1998 |
| WO 9706235 | A | 20-02-1997 | CA | 2228966 A | 20-02-1997 |
| | | | EP | 0843719 A | 27-05-1998 |
| US 4915866 | A | 10-04-1990 | US | 4775720 A | 04-10-1988 |
| | | | US | 4839083 A | 13-06-1989 |
| | | | US | 4840801 A | 20-06-1989 |
| | | | US | 4824828 A | 25-04-1989 |
| | | | US | 4865853 A | 12-09-1989 |